Supplementary Information

Late-stage oxidative C(sp^3)–H methylation

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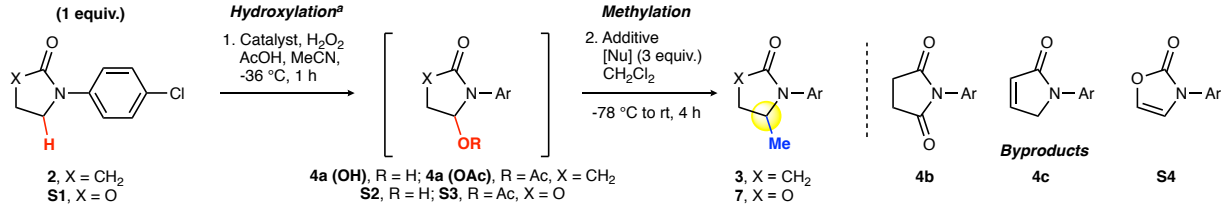
I. General information

All C–H oxidations were run under air with no precautions taken to exclude moisture. All other reactions were run under nitrogen atmosphere with dry solvent in flame-dried glassware unless otherwise noted. Dry solvents tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), dimethylsulfoxide (DMSO), and acetonitrile (MeCN) were purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, CA). Commercially available reagents that were used as received are noted in the individual reaction procedures. Trimethylaluminum ($AlMe_3$), DAST, TFAA, and BF_3•OEt_2 were purchased from Millipore-Sigma. TMSOTf was purchased from Oakwood Chemical. (*R,R*)- and (*S,S*)-Fe(PDP)[1], Fe(CF_3PDP)[2], Mn(CF_3PDP) **1**[3], Mn(PDP)[3], and Mn(PDP)$(OTf)_2$[4] were prepared according to literature procedures and stored in the fridge. Prior to use, catalysts were warmed to room temperature and weighed out in air. Thin-layer chromatography (TLC) was conducted with E. Merck TLC silica gel 60 F_{254} pre-coated plates (0.25 mm) or E. Merck TLC aluminum oxide 60 F_{254}, basic, pre-coated glass backed plates. Visualization was conducted with UV, CAM stain, and potassium permanganate ($KMnO_4$) stain. Flash chromatography was performed using ZEOprep 60 ECO 43-60 micron silica gel (American International Chemical, Inc.) or basic aluminum oxide, Brockmann grade III (6% H_2O added to Brockmann grade I) prepared from Alfa Aesar aluminum oxide, activated, basic, Brockmann grade I, 58 angstroms, 60 mesh power, S.A. 150m^2/g, CAS: 1344-28-1. Medium pressure liquid chromatography was performed on a Teledyne Isco CombiFlash Rf machine using pre-packed RediSep columns.

^{1}H-NMR spectra were recorded on a Varian Unity Inova 400 (400 MHz), Varian VXR 500 (500 MHz), Varian Unity 500 (500 MHz), or Carver-Bruker 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sxt = sextet, hept = septet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Unity 500 (125 MHz) or Carver-Bruker 500 (125MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). ^{19}F spectra were recorded on a Varian Unity-500 (470 MHz), Varian Unity-500 (470 MHz) or Carver-Bruker 500 (470 MHz) and are reported in ppm using $FCCl_3$ (0 ppm) as an external standard. Labeled solvent impurities were calculated out when reporting isolated yields. High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Electrospray ionization (ESI) spectra were performed on a Waters Q-Tof μLtima spectrometer.

II. Optimization data

Table 1 | Development of Mn(CF_3PDP) **1**-mediated oxidative methylation



2, X = CH_2; **S1**, X = O

4a (OH), R = H; **4a (OAc)**, R = Ac, X = CH_2; **S2**, R = H; **S3**, R = Ac, X = O

3, X = CH_2; **7**, X = O

4b **4c** **S4**

Entry	Substr.	Catalyst	Loading (mol%)	Additive	[Nu]	**4a (OH)/ S2** (%)	**4a (OAc)/ S3** (%)	**3/7** (%)	**4b** (%)	**4c/S4** (%)	rsm (%)
Oxidation											
1[b]	**2**	Fe(PDP)	3 x 5	-	-	<5[k]	0	-	<5[k]	-	0
2[c]	**2**	Fe(CF_3PDP)	3 x 5	-	-	8[k]	0	-	6[k]	-	0
3[d]	**2**	Mn(PDP)($OTf)_2$	1	-	-	12	0	-	0	-	75
4	**2**	Mn(PDP)($SbF_6)_2$	1	-	-	28	7	-	<5[k]	-	35
5[e]	**2**	Mn(CF_3PDP) **1**	10	-	-	13[k]	10	-	41	-	0
6	**2**	**1**	1	-	-	51	21	-	9	-	0
7	**2**	**1**	0.5	-	-	64	18	-	<5[k]	-	4
Methylation											
8[f]	**2**	**1**	0.5	BF_3•OEt_2	$AlMe_3$	<5[k]	0	63	<5[k]	0	11
9[f]	**S1**	**1**	0.5	BF_3•OEt_2	$AlMe_3$	11	5	10	-	4	27
10[g]	**S1**	**1**	0.5	DAST	$AlMe_3$	0	14[k]	55	-	0	16
11[g]	**2**	**1**	0.5	DAST	$AlMe_3$	0	0	64	<5[k]	0	12
12[g]	**2**	**1**	0.5	Deoxo-Fluor	$AlMe_3$	0	0	61	6	0	5
13[h]	**2**	**1**	0.5	TFAA/ TMSOTf	$AlMe_3$	0	0	51	<5[k]	14	9
14[h]	**S1**	**1**	0.5	TFAA/ TMSOTf	$AlMe_3$	0	0	46	-	20	13
15[i]	**2**	**1**	0.5	MsCl/Et_3N	$AlMe_3$	15	0	0	<5[k]	39	6
16[g]	**2**	**1**	0.5	DAST	$ZnMe_2$	17	9	0	11	0	14
17[g,j]	**2**	**1**	0.5	DAST	MeMgBr	24	<5[k]	24	<5[k]	0	9

Extended Data Table 1. Reaction optimization. [a]General oxidation (unless otherwise noted): **2** (0.3 mmol), catalyst (x mol%, (*R*,*R*) and (*S*,*S*) used interchangeably), AcOH (15 equiv.), MeCN (0.5 M), -36 °C; H_2O_2 (2 equiv.) in MeCN (3.75 mL) syringe pump 1 h. Mixture passed through silica plug, EtOAc flush, concentrated prior to isolation or methylation. Isolated product yields. [b] Procedure ref. 28. [c] Procedure ref. 29. [d]Procedure ref. 31. [e]5 equiv. H_2O_2. [f]General BF_3 alkylation: crude in CH_2Cl_2 (0.2 M), -78 °C, $AlMe_3$ (3 equiv.) and BF_3•OEt_2 (2 equiv.) sequentially added, stirred 1 h; room temperature (rt) for 3 h. [g]General fluorine alkylation: crude in CH_2Cl_2 (0.2 M), fluorine additive (1 equiv.) added at -78 °C; rt for 1 h; cooled to -78 °C, nucleophile (3 equiv.) added, stirred 2 h; rt for 1 h. [h]General TMSOTf alkylation: crude in CH_2Cl_2 (0.2 M), TFAA (1 equiv.) added, stirred 1 h; cooled to -78 °C, $AlMe_3$ (3 equiv.) and TMSOTf (1 equiv.) sequentially added, stirred 2 h; rt for 1 h. [i]Crude in CH_2Cl_2 (0.2 M), MsCl (1 equiv.) and Et_3N (1 equiv.) added, stirred 1 h; washed $NaHCO_3$, dried, reduced; redissolved in CH_2Cl_2, $AlMe_3$ (3 equiv.) added at -78 °C, stirred 2 h; rt for 1 h. [j]MeMgBr (3 equiv.) added at -78°C, stirred 3 h. [k]Yield by crude ^{1}H NMR.

Procedure A for reaction optimization studies (substrate oxidation)

In a 40 mL vial the starting material (0.30 mmol, 1.0 equiv.) and the catalyst ((*R*,*R*)- and (*S*,*S*)-enantiomers were used interchangeably for achiral substrates) were dissolved in MeCN (0.6 mL, 0.50 M). AcOH (256 µL, 4.50 mmol, 15.0 equiv.) was then added. A 10 mL syringe was charged with a solution of H_2O_2 (34.3 µL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.16 M), and fitted with a 25G needle. The vial was sealed with a screw cap fitted with a PTFE/Silicone septum and cooled to -36 °C with a 1,2-DCE/dry ice bath. The H_2O_2 solution was added into the stirring reaction mixture via a syringe pump at 3.75 mL/h. Upon completion, the reaction mixture was added via syringe onto a 15 mL silica plug and allowed to sit for 5 min to ensure complete H_2O_2 consumption. EtOAc (150 mL) was then allowed to pass through the silica plug. The resulting solution was condensed under vacuum and purified by flash chromatography (50 mL silica, 20%→30%→40%→50%→75% EtOAc/Hex).

Procedure B for reaction optimization studies (BF_3-assisted methylation)

The starting material was oxidized according to procedure A for reaction optimization studies. Upon passing through the silica plug, the resulting solution was condensed and transferred into a 25 mL recovery flask. The solvents were removed through rotary evaporation, and the residual acetic acid was removed under vacuum overnight. The crude was backfilled with nitrogen 3x, redissolved in CH_2Cl_2 (1.5 mL), and cooled to -78 °C with an acetone/dry ice bath. Trimethylaluminum (2 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.) was added dropwise, followed by boron trifluoride diethyl ether complex (74.1 µL, 0.60 mmol, 2.0 equiv.). The mixture was stirred at -78 °C for 1 h, then allowed to gradually warm up while further stirring for 3 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and poured into a 60 mL separatory funnel with 5 mL 1 M NaOH. The aqueous layer was extracted with CH_2Cl_2 twice and the organic layers were combined, dried over $MgSO_4$, filtered, condensed, and purified by flash chromatography (50 mL silica, 10%→20%→30% EtOAc/Hex).

Procedure C for reaction optimization studies (fluorine-assisted methylation)

The starting material was oxidized according to procedure A for reaction optimization studies. Upon passing through the silica plug, the resulting solution was condensed and transferred into a 25 mL recovery flask. The solvents were removed through rotary evaporation, and the residual acetic acid was removed under vacuum overnight. The crude was backfilled with nitrogen 3x, redissolved in CH_2Cl_2 (1.5 mL), and cooled to -78 °C with an acetone/dry ice bath. The fluorinating reagent (0.30 mmol, 1.0 equiv.) was added, and the reaction was allowed to warm up to room temperature while stirring for 1 h. The flask was then again placed in -78 °C cold bath, and trimethylaluminum (2 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.) was added dropwise. The mixture was stirred at -78 °C for 2 h, then allowed to gradually

warm up while further stirring for 1 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and poured into a 60 mL separatory funnel with 5 mL 1 M NaOH. The aqueous layer was extracted with CH_2Cl_2 twice and the organic layers were combined, dried over $MgSO_4$, filtered, condensed, and purified by flash chromatography (50 mL silica, 10%→20%→30% EtOAc/Hex).

Entry 1. According to literature[5], **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) in a 40 mL vial was dissolved in MeCN (0.6 mL). The vial was placed into an ice bath and allowed to stir for 30 s, and AcOH (8.6 μL, 0.15 mmol, 0.5 equiv.) was added, followed by a solution of Fe(PDP) (14.0 mg, 0.015 mmol, 0.05 equiv.) in MeCN (0.3 mL). A solution of H_2O_2 (35.0 μL, 0.57 mmol, 1.9 equiv., 50 wt.% in H_2O) in MeCN (4.5 mL) at 0 °C was added dropwise via a pipet to the stirring solution over 2-3 minutes. After 10 min, a second portion of AcOH and Fe(PDP) were added to the reaction mixture, followed by the dropwise addition of a second portion of H_2O_2 solution in MeCN as described above. After an additional 10 minutes, a third portion of Fe(PDP) and AcOH dissolved in MeCN were added followed by the dropwise addition of a third portion of H_2O_2 solution in MeCN as described above. The reaction solution was stirred for 10 minutes after the last iterative addition, for a total reaction time of approximately 36 minutes. Upon completion, the reaction mixture was added via syringe onto a 15 mL silica plug and allowed to sit for 5 min to ensure complete H_2O_2 consumption. EtOAc (150 mL) was then allowed to pass through the silica plug. The resulting solution was condensed under vacuum.

Run 1 (trace **4a (OH)** by ^{1}H NMR; trace **4b** by ^{1}H NMR; 0% rsm)

Run 2 (trace **4a (OH)** by ^{1}H NMR; trace **4b** by ^{1}H NMR; 0% rsm)

Run 3 (trace **4a (OH)** by ^{1}H NMR; trace **4b** by ^{1}H NMR; 0% rsm)

Average overall yield: Trace 4a (OH) and 4b, 0% RSM

Entry 2. According to literature[5], **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) in a 40 mL vial was dissolved in MeCN (0.6 mL). The vial was placed into an ice bath and allowed to stir for 30 s, and AcOH (8.6 μL, 0.15 mmol, 0.5 equiv.) was added, followed by a solution of Fe(CF_3PDP) (20.3 mg, 0.015 mmol, 0.05 equiv.) in MeCN (0.3 mL). A solution of H_2O_2 (35.0 μL, 0.57 mmol, 1.9 equiv., 50 wt.% in H_2O) in MeCN (4.5 mL) at 0 °C was added dropwise via a pipet to the stirring solution over 2-3 minutes. After 10 min, a second portion of AcOH and Fe(CF_3PDP) were added to the reaction mixture, followed by the dropwise addition of a second portion of H_2O_2 solution in MeCN as described above. After an additional 10 minutes, a third portion of Fe(CF_3PDP) and AcOH dissolved in MeCN were added followed by the dropwise addition of a third portion of H_2O_2 solution in MeCN as described above. The reaction solution was stirred for 10 minutes after the last iterative addition, for a total reaction time of approximately 36 minutes. Upon completion, the reaction mixture was added via syringe onto a 15 mL silica plug and

allowed to sit for 5 min to ensure complete H_2O_2 consumption. EtOAc (150 mL) was then allowed to pass through the silica plug. The resulting solution was condensed under vacuum.

Run 1 (8% **4a (OH)** by ^{1}H NMR; 6% **4b** by ^{1}H NMR; 0% rsm)

Run 2 (7% **4a (OH)** by ^{1}H NMR; 6% **4b** by ^{1}H NMR; 0% rsm)

Run 3 (10% **4a (OH)** by ^{1}H NMR; 6% **4b** by ^{1}H NMR; 0% rsm)

Average overall yield: 8% 4a (OH), 6% 4b, 0% RSM

Entry 3. According to literature[4], **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) and Mn(PDP)$(OTf)_2$ (2.0 mg, 0.003 mmol, 0.01 equiv.) were dissolved in MeCN (1.2 mL, 0.25 M). AcOH (223 µL, 3.90 mmol, 13.0 equiv.) was then added. A 10 mL syringe was charged with a solution of H_2O_2 (60.1 µL, 1.05 mmol, 3.5 equiv, 30 wt.% in H_2O) in MeCN (0.7 mL, 1.5 M), and fitted with a 25G needle. The vial was sealed with a screw cap fitted with a PTFE/Silicone septum and cooled to -40 °C with an acetonitrile/dry ice bath. The H_2O_2 solution was added into the stirring reaction mixture via a syringe pump at 1.40 mL/h. Upon completion, the reaction mixture was added via syringe onto a 15 mL silica plug. EtOAc (150 mL) was then allowed to pass through the silica plug. The resulting solution was condensed under vacuum and purified by flash chromatography (50 mL silica, 10%→20%→30% EtOAc/Hex).

Run 1 (6.6 mg, 0.031 mmol, 10% **4a (OH)**; 41.6 mg, 0.213 mmol, 71% rsm)

Run 2 (9.4 mg, 0.044 mmol, 15% **4a (OH)**; 47.0 mg, 0.240 mmol, 80% rsm)

Run 3 (7.7 mg, 0.036 mmol, 12% **4a (OH)**; 44.3 mg, 0.227 mmol, 75% rsm)

Average overall yield: 12% 4a (OH), 75% RSM

Entry 4. According to procedure A for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using Mn(PDP)$(MeCN)_2(SbF_6)_2$ (2.8 mg, 0.003 mmol, 0.01 equiv.).

Run 1 (20.2 mg, 0.0954 mmol, 32% **4a (OH)**; 2.5 mg, 0.0099 mmol, 3% **4a (OAc)**; trace **4b** by ^{1}H NMR; 17.7 mg, 0.0906 mmol, 30% rsm)

Run 2 (19.0 mg, 0.0817 mmol, 27% **4a (OH)**; 7.4 mg, 0.029 mmol, 10% **4a (OAc)**; trace **4b** by ^{1}H NMR; 19.1 mg, 0.0976 mmol, 33% rsm)

Run 3 (16.7 mg, 0.0787 mmol, 26% **4a (OH)**; 5.1 mg, 0.020 mmol, 7% **4a (OAc)**; trace **4b** by ^{1}H NMR; 25.0 mg, 0.128 mmol, 43% rsm)

Average overall yield: 28% 4a (OH), 7% 4a (OAc), trace 4b, 35% RSM

Entry 5. According to procedure A for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using Mn$(CF_3PDP)(MeCN)_2(SbF6)_2$ (40.7 mg, 0.03 mmol, 0.1 equiv.) and H_2O_2 (85.8 µL, 1.50 mmol, 5.0 equiv., 50 wt.% in H_2O).

Run 1 (16% **4a (OH)** by ^{1}H NMR; 7.9 mg, 0.031 mmol, 10% **4a (OAc)**; 23.7 mg, 0.118 mmol, 39% **4b**; 0% rsm)
Run 2 (10% **4a (OH)** by ^{1}H NMR; 7.7 mg, 0.030 mmol, 10% **4a (OAc)**; 26.6 mg, 0.127 mmol, 42% **4b**; 0% rsm)

Average overall yield: 13% 4a (OH), 10% 4a (OAc), 41% 4b, 0% RSM

Entry 6. According to procedure A for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (4.1 mg, 0.003 mmol, 0.01 equiv.).
Run 1 (31.9 mg, 0.151 mmol, 50% **4a (OH)**; 14.3 mg, 0.0564 mmol, 19% **4a (OAc)**; 9.7 mg, 0.038 mmol, 13% **4b**; 0% rsm)
Run 2 (33.9 mg, 0.160 mmol, 53% **4a (OH)**; 19.2 mg, 0.0755 mmol, 25% **4a (OAc)**; 5.7 mg, 0.0272 mmol, 9% **4b**; 0% rsm)
Run 3 (31.3 mg, 0.148 mmol, 49% **4a (OH)**; 14.6 mg, 0.0574 mmol, 19% **4a (OAc)**; 3.2 mg, 0.015 mmol, 5% **4b**; 0% rsm)

Average overall yield: 51% 4a (OH), 21% 4a (OAc), 9% 4b, 0% RSM

Entry 7. According to procedure A for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.).
Run 1 (39.0 mg, 0.184 mmol, 61% **4a (OH)**; 17.2 mg, 0.0681 mmol, 23% **4a (OAc)**; trace **4b** by ^{1}H NMR; 2.7 mg, 0.014 mmol, 5% rsm)
Run 2 (42.2 mg, 0.199 mmol, 66% **4a (OH)**; 13.0 mg, 0.0513 mmol, 17% **4a (OAc)**; trace **4b** by ^{1}H NMR; 4.7 mg, 0.024 mmol, 8% rsm)
Run 3 (41.5 mg, 0.196 mmol, 66% **4a (OH)**; 11.5 mg, 0.0543 mmol, 15% **4a (OAc)**; trace **4b** by ^{1}H NMR; 0% rsm)

Average overall yield: 64% 4a (OH), 18% 4a (OAc), trace 4b, 4% RSM

Entry 8. According to procedure B for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was methylated using BF_3•OEt_2 and $AlMe_3$ as described.
Run 1 (trace **4a (OH)** by ^{1}H NMR; 37.2 mg, 0.177 mmol, 59% **3**; trace **4b** by ^{1}H NMR; 9.9 mg, 0.051 mmol, 17% rsm)
Run 2 (41.8 mg, 0.199 mmol, 66% **3**; trace **4b** by ^{1}H NMR; 4.1 mg, 0.021 mmol, 7% rsm)
Run 3 (41.2 mg, 0.196 mmol, 65% **3**; trace **4b** by ^{1}H NMR; 5.3 mg, 0.027 mmol, 9% rsm)

Average overall yield: trace 4a (OH), 63% of 3, trace 4b, 11% RSM

Entry 9. According to procedure B for optimization studies, **S1** (59.3 mg, 0.30 mmol, 1.0 equiv.) was methylated using BF_3•OEt_2 and $AlMe_3$ as described.
Run 1 (3.5 mg, 0.015 mmol, 5% **S2**; 6.6 mg, 0.026 mmol, 9% **S3**; 6.2 mg, 0.029 mmol, 10% **7**; 3.3 mg, 0.017 mmol, 6% **S4**; 14.0 mg, 0.0708 mmol, 24% rsm)
Run 2 (10.9 mg, 0.0510 mmol, 17% **S2**; 0.8 mg, 0.003 mmol, 1% **S3**; 6.1 mg, 0.029 mmol, 10% **7**; 1.7 mg, 0.0087 mmol, 3% **S4**; 18.3 mg, 0.0925 mmol, 31% rsm)
Run 3 (6.3 mg, 0.029 mmol, 10% **S2**; 3.8 mg, 0.015 mmol, 5% **S3**; 7.2 mg, 0.034 mmol, 11% **7**; 1.6 mg, 0.0082 mmol, 3% **S4**; 15.3 mg, 0.0774 mmol, 26% rsm)

Average overall yield: 11% S2, 5% S3, 10% 7, 4% S4, 27% RSM

Entry 10. According to procedure C for optimization studies, **S1** (59.3 mg, 0.30 mmol, 1.0 equiv.) was methylated using DAST (39.6 μL, 0.30 mmol, 1.0 equiv.) and $AlMe_3$ as described.
Run 1 (14% **S3** by ^{1}H NMR; 35.9 mg, 0.170 mmol, 57% **7**; 6.0 mg, 0.030 mmol, 10% rsm)
Run 2 (17% **S3** by ^{1}H NMR; 35.3 mg, 0.167 mmol, 56% **7**; 6.6 mg, 0.033 mmol, 11% rsm)
Run 3 (10% **S3** by ^{1}H NMR; 33.2 mg, 0.157 mmol, 52% **7**; 15.8 mg, 0.0800 mmol, 27% rsm)

Average overall yield: 14% S3, 55% 7, 16% RSM

Entry 11. According to procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was methylated using DAST (39.6 μL, 0.30 mmol, 1.0 equiv.) and $AlMe_3$ as described.
Run 1 (38.3 mg, 0.183 mmol, 61% **3**; trace **4b** by ^{1}H NMR; 7.2 mg, 0.037 mmol, 12% rsm)
Run 2 (42.1 mg, 0.201 mmol, 67% **3**; trace **4b** by ^{1}H NMR; 4.1 mg, 0.021 mmol, 7% rsm)
Run 3 (39.9 mg, 0.190 mmol, 63% **3**; trace **4b** by ^{1}H NMR; 10.0 mg, 0.0511 mmol, 17% rsm)

Average overall yield: 64% of 3, trace 4b, 12% RSM

Entry 12. According to procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was methylated using Deoxo-Fluor (55.3 μL, 0.30 mmol, 1.0 equiv.) and $AlMe_3$ as described.
Run 1 (38.2 mg, 0.182 mmol, 61% **3**; 7.6 mg, 0.036 mmol, 12% **4b** by ^{1}H NMR; 0% rsm)
Run 2 (38.7 mg, 0.185 mmol, 62% **3**; 1.8 mg, 0.0086 mmol, 3% **4b**; 2.8 mg, 0.014 mmol, 5% rsm)
Run 3 (38.6 mg, 0.184 mmol, 61% **3**; 1.3 mg, 0.0060 mmol, 2% **4b**; 5.3 mg, 0.027 mmol, 9% rsm)

Average overall yield: 61% of 3, 6% 4b, 5% RSM

Entry 13. According to a modified procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.) and worked up as described. The crude was backfilled with nitrogen 3x and redissolved in CH_2Cl_2 (1.5 mL). Trifluoroacetic anhydride (41.7 μL, 0.3 mmol, 1.0 equiv.) was added at room temperature, and the

reaction was stirred for 1 h. The reaction flask was then placed in a -78 °C acetone/dry ice bath, and trimethylaluminum (2 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was added dropwise, followed by TMSOTf (54.3 μL, 0.30 mmol, 1.0 equiv.). The mixture was stirred at -78 °C for 2 h, then allowed to gradually warm up while further stirring for 1 h before quenching as described.

Run 1 (32.0 mg, 0.153 mmol, 51% **3**; trace **4b** by ^{1}H NMR; 9.5 mg, 0.049 mmol, 16% **4c**; 4.3 mg, 0.022 mmol, 7% rsm)

Run 2 (34.2 mg, 0.163 mmol, 54% **3**; trace **4b** by ^{1}H NMR; 7.6 mg, 0.039 mmol, 13% **4c**; 7.1 mg, 0.036 mmol, 11% rsm)

Run 3 (31.0 mg, 0.148 mmol, 49% **3**; trace **4b** by ^{1}H NMR; 7.0 mg, 0.036 mmol, 12% **4c**; 4.7 mg, 0.024 mmol, 8% rsm)

Average overall yield: 51% of 3, trace 4b, 14% 4c, 9% RSM

Entry 14. According to a modified procedure C for optimization studies, **S1** (59.3 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.) and worked up as described. The crude was backfilled with nitrogen 3x and redissolved in CH_2Cl_2 (1.5 mL). Trifluoroacetic anhydride (41.7 μL, 0.3 mmol, 1.0 equiv.) was added at room temperature, and the reaction was stirred for 1 h. The reaction flask was then placed in a -78 °C acetone/dry ice bath, and trimethylaluminum (2 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was added dropwise, followed by TMSOTf (54.3 μL, 0.30 mmol, 1.0 equiv.). The mixture was stirred at -78 °C for 2 h, then allowed to gradually warm up while further stirring for 1 h before quenching as described.

Run 1 (26.8 mg, 0.127 mmol, 42% **7**; 9.7 mg, 0.050 mmol, 17% **S4**; 9.6 mg, 0.049 mmol, 16% rsm)

Run 2 (28.1 mg, 0.133 mmol, 44% **7**; 11.5 mg, 0.0588 mmol, 20% **S4**; 5.4 mg, 0.027 mmol, 9% rsm)

Run 3 (33.1 mg, 0.156 mmol, 52% **7**; 14.2 mg, 0.0726 mmol, 24% **S4**; 7.3 mg, 0.044 mmol, 15% rsm)

Average overall yield: 46% of 7, 20% S4, 13% RSM

Entry 15. According to a modified procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.) and worked up as described. The crude was backfilled with nitrogen 3x and redissolved in CH_2Cl_2 (1.5 mL). MsCl (23.2 μL, 0.3 mmol, 1.0 equiv.) and Et_3N (41.8 μL, 0.3 mmol, 1.0 equiv.) were added at room temperature, and the reaction was stirred for 1 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, and poured into a 60 mL separatory funnel containing 5 mL $NaHCO_3$. The aqueous layer was extracted with 5 mL CH_2Cl_2 2x, and the organic layers were combined, dried over MgSO4, condensed under vacuum, and transferred back into the 25 mL recovery flask. The crude was backfilled with N2 3x and 1.5 mL CH_2Cl_2 was added. The reaction flask was then placed in a -78 °C acetone/dry ice bath, and

trimethylaluminum (2 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was added dropwise. The mixture was stirred at -78 °C for 2 h, then allowed to gradually warm up while further stirring for 1 h before quenching as described.

Run 1 (11.4 mg, 0.0539 mmol, 18% **4a (OH)**; trace **4b** by ^{1}H NMR; 19.7 mg, 0.102 mmol, 34% **4c**; 1.6 mg, 0.0082 mmol, 3% rsm)

Run 2 (12.1 mg, 0.0575 mmol, 19% **4a (OH)**; trace **4b** by ^{1}H NMR; 23.4 mg, 0.121 mmol, 40% **4c**; 2.5 mg, 0.013 mmol, 4% rsm)

Run 3 (4.5 mg, 0.021 mmol, 7% **4a (OH)**; trace **4b** by ^{1}H NMR; 24.6 mg, 0.127 mmol, 42% **4c**; 7.1 mg, 0.036 mmol, 12% rsm)

Average overall yield: 15% 4a (OH), trace 4b, 39% 4c, 6% RSM

Entry 16. According to a modified procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.) and worked up as described. The crude was backfilled with nitrogen 3x, redissolved in CH_2Cl_2 (1.5 mL), and cooled to -78 °C with an acetone/dry ice bath. DAST (39.6 μL, 0.30 mmol, 1.0 equiv.) was added, and the reaction was allowed to warm up to room temperature while stirring for 1 h. The flask was then again placed in -78 °C cold bath, and dimethylzinc (2 M in toluene, 450 μL, 0.90 mmol, 3.0 equiv.) was added dropwise. The mixture was stirred at -78 °C for 2 h, then allowed to gradually warm up while further stirring for 1 h before quenching as described.

Run 1 (5.6 mg, 0.026 mmol, 9% **4a (OH)**; 3.0 mg, 0.0018 mmol, 4% **4a (OAc)**; trace **4b** by ^{1}H NMR; 14.6 mg, 0.0745 mmol, 25% rsm)

Run 2 (15.3 mg, 0.0725 mmol, 24% **4a (OH)**; 6.9 mg, 0.027 mmol, 9% **4a (OAc)**; 10.8 mg, 0.0513 mmol, 17% **4b**; 0% rsm)

Run 3 (10.9 mg, 0.0513 mmol, 17% **4a (OH)**; 10.0 mg, 0.0393 mmol, 13% **4a (OAc)**; trace **3** by ^{1}H NMR; 10.8 mg, 0.0513 mmol, 17% **4b**; 10.6 mg, 0.0542 mmol, 18% rsm)

Average overall yield: 17% 4a (OH), 9% 4a (OAc), 11% 4b, 14% RSM

Entry 17. According to a modified procedure C for optimization studies, **2** (58.7 mg, 0.30 mmol, 1.0 equiv.) was oxidized using $Mn(CF_3PDP)(MeCN)_2(SbF_6)_2$ (2.0 mg, 0.0015 mmol, 0.005 equiv.) and worked up as described. The crude was backfilled with nitrogen 3x, redissolved in CH_2Cl_2 (1.5 mL), and cooled to -78 °C with an acetone/dry ice bath. DAST (39.6 μL, 0.30 mmol, 1.0 equiv.) was added, and the reaction was allowed to warm up to room temperature while stirring for 1 h. The flask was then again placed in -78 °C cold bath, and MeMgBr (3 M in THF, 300 μL, 0.90 mmol, 3.0 equiv.) was added

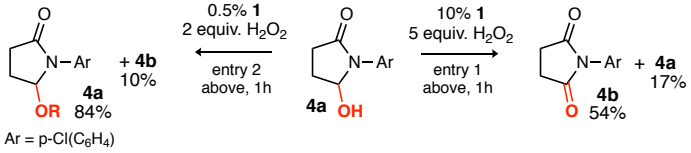
dropwise. The mixture was stirred at -78 °C for 3 h, then directly quenched with 1 M HCl (3 mL) without warming up.

Run 1 (17.8 mg, 0.0841 mmol, 28% **4a (OH)**; trace **4a (OAc)** by ^{1}H NMR; 14.9 mg, 0.0709 mmol, 24% **3;** trace **4b** by ^{1}H NMR; 1.8 mg, 0.0092 mmol, 3% rsm)

Run 2 (22.0 mg, 0.104 mmol, 35% **4a (OH)**; trace **4a (OAc)** by ^{1}H NMR; 16.3 mg, 0.0776 mmol, 26% **3;** trace **4b** by ^{1}H NMR; 7.6 mg, 0.039 mmol, 13% rsm)

Run 3 (5.4 mg, 0.026 mmol, 9% **4a (OH)**; 4.5 mg, 0.018 mmol, 6% **4a (OAc)**; 13.9 mg, 0.0664 mmol, 22% **3;** trace **4b** by ^{1}H NMR; 10.0 mg, 0.0511 mmol, 10% rsm)

Average overall yield: 24% 4a (OH), trace 4a (OAc), 24% of 3, trace 4b, 9% RSM



Oxidation of **4a (OH)** (42.3 mg, 0.20 mmol, 1.0 equiv.) with 0.5 mol% **1** and 2 equiv. H_2O_2:

Run 1 (4.8 mg, 0.023 mmol, 11% **4b**; 5.5 mg, 0.022 mmol, 11% **4a (OAc)**; 29.7 mg, 0.140 mmol, 70% rsm **4a (OH)**)

Run 2 (3.8 mg, 0.018 mmol, 9% **4b**; 7.6 mg, 0.030 mmol, 15% **4a (OAc)**; 30.3 mg, 0.143 mmol, 72% rsm **4a (OH)**)

Average yield: 10% imide 4b; 71% hemiaminal 4a (OH); 13% hemiaminal acetate 4a (OAc)

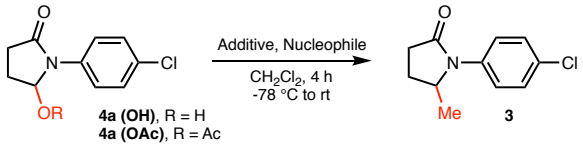
Oxidation of **4a (OH)** (42.3 mg, 0.20 mmol, 1.0 equiv.) with 10 mol% **1** and 5 equiv. H_2O_2:

Run 1 (21.4 mg, 0.102 mmol, 51% **4b**; 2.1 mg, 0.0082 mmol, 4% **4a (OAc)**; 13% rsm **4a (OH)** by ^{1}H NMR)

Run 2 (23.3 mg, 0.111 mmol, 56% **4b**; 4.2 mg, 0.017 mmol, 8% **4a (OAc)**; 9% rsm **4a (OH)** by ^{1}H NMR)

Average yield: 54% imide 4b; 11% hemiaminal 4a (OH); 6% hemiaminal acetate 4a (OAc)

Table 2 | Methylation efficiency study



Entry	Substrate	Additive (equiv.)	Nucleophile (equiv.)	**3**, %	rsm, %

1	**4a (OH)**	BF_3•OEt_2 (2)	$AlMe_3$ (3)	60	15
2	**4a (OH)**	BF_3•OEt_2 (3.3)	$AlMe_3$ (5)	64	11
3	**4a (OAc)**	BF_3•OEt_2 (2)	$AlMe_3$ (3)	86	0
4	**4a (OAc)**	BF_3•OEt_2 (3.3)	$AlMe_3$ (5)	92	0
5	**4a (OH)**	DAST (1)	$AlMe_3$ (3)	81	0
6	**4a (OH)**	DAST (1.7)	$AlMe_3$ (5)	87	0
7	**4a (OAc)**	DAST (1)	$AlMe_3$ (3)	78	0
8	**4a (OAc)**	DAST (1.7)	$AlMe_3$ (5)	85	0

Entry 1. According to general procedure B for optimization studies, **4a (OH)** (21.2 mg, 0.10 mmol, 1.0 equiv.) was methylated using BF_3• OEt_2 (24.7 µL, 0.20 mmol, 2.0 equiv.) and $AlMe_3$ (2 M, 150 µL, 0.30 mmol, 3.0 equiv.) as described. Starting material did not fully dissolve and likely contributed to lower conversion.

Run 1 (12.6 mg, 0.0601 mmol, 60% **3**; 3.1 mg, 0.0146 mmol, 15% rsm)

Entry 2. According to general procedure B for optimization studies, assuming a 60% oxidation yield to mimic reagent equivalences for a one-pot procedure, **4a (OH)** (21.2 mg, 0.10 mmol, 1.0 equiv.) was methylated using BF_3•OEt_2 (40.7 µL, 0.33 mmol, 3.3 equiv.) and $AlMe_3$ (2 M, 250 µL, 0.50 mmol, 5.0 equiv.) in 0.5 mL CH_2Cl_2 as described. Starting material did not fully dissolve and likely contributed to lower conversion.

Run 1 (13.5 mg, 0.0644 mmol, 64% **3**; 2.3 mg, 0.0108 mmol, 11% rsm)

Entry 3. According to general procedure B for optimization studies, **4a (OAc)** (25.4 mg, 0.10 mmol, 1.0 equiv.) was methylated using BF_3• OEt_2 (24.7 µL, 0.20 mmol, 2.0 equiv.) and $AlMe_3$ (2 M, 150 µL, 0.30 mmol, 3.0 equiv.) as described.

Run 1 (18.0 mg, 0.0858 mmol, 86% **3**; 0% rsm)

Entry 4. According to general procedure B for optimization studies, assuming a 60% oxidation yield to mimic reagent equivalences for a one-pot procedure, **4a (OAc)** (25.4 mg, 0.10 mmol, 1.0 equiv.) was methylated using BF_3•OEt_2 (40.7 µL, 0.33 mmol, 3.3 equiv.) and $AlMe_3$ (2 M, 250 µL, 0.50 mmol, 5.0 equiv.) in 0.5 mL CH_2Cl_2 as described.

Run 1 (19.4 mg, 0.0924 mmol, 92% **3**; 0% rsm)

Entry 5. According to general procedure C for optimization studies, **4a (OH)** (21.2 mg, 0.10 mmol, 1.0 equiv.) was methylated using DAST (13.2 µL, 0.10 mmol, 1.0 equiv.) and $AlMe_3$ (2 M, 150 µL, 0.30 mmol, 3.0 equiv.) as described.

Run 1 (17.0 mg, 0.0811 mmol, 81% **3**; 0% rsm)

Entry 6. According to general procedure C for optimization studies, assuming a 60% oxidation yield to mimic reagent equivalences for a one-pot procedure, **4a (OH)** (21.2 mg, 0.10 mmol, 1.0 equiv.) was methylated using DAST (22.4 μL, 0.17 mmol, 1.7 equiv.) and $AlMe_3$ (2 M, 250 μL, 0.50 mmol, 5.0 equiv.) in 0.5 mL CH_2Cl_2 as described.

Run 1 (18.2 mg, 0.0868 mmol, 87% **3**; 0% rsm)

Entry 7. According to general procedure C for optimization studies, **4a (OAc)** (25.4 mg, 0.10 mmol, 1.0 equiv.) was methylated using DAST (13.2 μL, 0.10 mmol, 1.0 equiv.) and $AlMe_3$ (2 M, 150 μL, 0.30 mmol, 3.0 equiv.) as described.

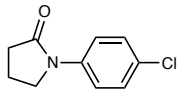
Run 1 (16.4 mg, 0.0782 mmol, 78% **3**; 0% rsm)

Entry 8. According to general procedure C for optimization studies, assuming a 60% oxidation yield to mimic reagent equivalences for a one-pot procedure, **4a (OAc)** (25.4 mg, 0.10 mmol, 1.0 equiv.) was methylated using DAST (22.4 μL, 0.17 mmol, 1.7 equiv.) and $AlMe_3$ (2 M, 250 μL, 0.50 mmol, 5.0 equiv.) in 0.5 mL CH_2Cl_2 as described.

Run 1 (17.9 mg, 0.0854 mmol, 85% **3**; 0% rsm)

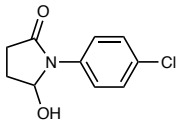
All entries suggest mostly similar yields and conversions between stoichiometric and one-pot equivalences of activators and trimethylaluminum. However, the one-pot equivalences produce slightly higher yields and are recommended for carrying out the methylation.

On the conversion of hemiaminal acetate: The hemiaminal acetate of lactam **2** and other heterocyclic cores have been observed to react with BF_3 and DAST to furnish methylated products (vide supra, Table 1); however, with carbamate substrates like **S1**, hemiaminal acetates do not react effectively (Table 1, entry 10, 14% **S3**).



1-(4-chlorophenyl)pyrrolidin-2-one [2]

Prepared according to literature procedures and the NMR data matched those reported[6].



1-(4-chlorophenyl)-5-hydroxypyrrolidin-2-one [4a (OH)]

^{1}H NMR: (500 MHz, $CDCl_3$)

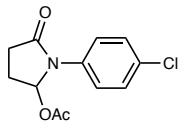
δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 5.63 (br s, 1H), 3.18 (br s, 1H), 2.83-2.69 (m, 1H), 2.53-2.38 (m, 2H), 2.09-2.00 (m, 1H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 174.35, 135.86, 131.67, 129.33, 124.50, 85.21, 29.75, 28.38

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{10}H_{11}NO_2Cl$ $[M+H]^+$: 212.0478, found 212.0482.



1-(4-chlorophenyl)-5-oxopyrrolidin-2-yl acetate [4a (OAc)]

^{1}H NMR: (500 MHz, $CDCl_3$)

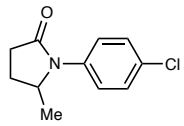
δ 7.38 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 9.2 Hz, 2H), 6.60 (d, *J* = 5.8 Hz, 1H), 2.87-2.70 (m, 1H), 2.61-2.42 (m, 2H), 2.19-2.10 (m, 1H), 2.05 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 174.82, 170.36, 135.45, 132.05, 129.41, 124.43, 86.04, 29.41, 26.46, 21.24

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{10}H_9NOCl$ $[M-Ac]^+$: 194.0373, found 194.0364.



1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one [3]

^{1}H NMR: (500 MHz, $CDCl_3$)

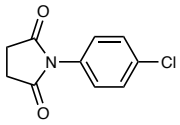
δ 7.37-7.29 (m, 4H), 4.27 (sxt, *J* = 6.1 Hz, 1H), 2.63 (ddd, *J* = 17.2, 9.5, 6.2 Hz, 1H), 2.52 (ddd, *J* = 17.0, 9.5, 7.1 Hz, 1H), 2.36 (ddt, *J* = 13.5, 9.5, 7.2 Hz, 1H), 1.79-1.69 (m, 1H), 1.20 (d, *J* = 6.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 174.29, 136.27, 130.98, 129.16, 125.02, 55.53, 31.36, 26.72, 20.12

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{13}NOCl$ $[M+H]^+$: 210.0686, found 210.0686.

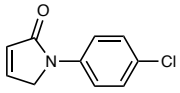


1-(4-chlorophenyl)pyrrolidine-2,5-dione [4b]

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 2.89 (s, 4H)

These data matched those reported in the literature[7].



1-(4-chlorophenyl)-1,5-dihydro-2*H*-pyrrol-2-one [4c]

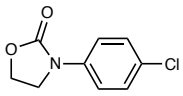
^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.68 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.19 (dt, *J* = 6.1, 2.0 Hz, 1H), 6.28 (dt, *J* = 6.1, 2.0 Hz, 1H), 4.43 (t, *J* = 2.0 Hz, 2H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.21, 142.35, 137.86, 129.40, 129.27, 129.22 120.01, 53.24

These data matched those reported in the literature[8].

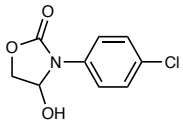


3-(4-chlorophenyl)oxazolidin-2-one [S1] In a 100 mL recovery flask were added 2-oxazolidinone (523 mg, 6.0 mmol, 1.2 equiv.), 1-chloro-4-iodobenzene (1.19 g, 5.0 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 0.01 equiv.), XantPhos (86.8 mg, 0.15 mmol, 0.03 equiv.), and potassium phosphate (1.49 g, 7.0 mmol, 1.4 equiv.). A reflux condenser was placed on the flask, and the system was refilled with argon 3x. 1,4-dioxane (30 mL) was then added, and the mixture was refluxed in 100 °C oil bath overnight under nitrogen atmosphere. Upon completion, the reaction was diluted with CH_2Cl_2 and passed through a Celite plug. The resulting solution was condensed in vacuo and purification via flash chromatography yielded the product as a pale yellow powder (818 mg, 4.14 mmol, 83% yield).

^{1}H NMR: (400 MHz, $CHCl_3$)

δ 7.50 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 9.1 Hz, 2H), 4.50 (dd, *J* = 8.7, 7.2 Hz, 2H), 4.04 (dd, *J* = 8.8, 7.2 Hz, 2H)

These data matched those reported in the literature[49].



3-(4-chlorophenyl)-4-hydroxyoxazolidin-2-one [S2]

^{1}H NMR: (400 MHz, CD_3CN)

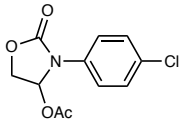
δ 7.59 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 9.1 Hz, 2H), 5.79-5.72 (m, 1H), 4.75 (d, *J* = 8.1 Hz, 1H), 4.51 (dd, *J* = 9.9, 6.2 Hz, 1H), 4.15 (dd, *J* = 9.9, 1.8 Hz, 1H)

^{13}C NMR: (126 MHz, CD_3CN)

δ 155.71, 136.87, 130.81, 129.81, 124.04, 81.20, 71.31

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_9H_9NO_3Cl$ $[M+H]^+$: 214.0271, found 214.0278.



3-(4-chlorophenyl)-2-oxooxazolidin-4-yl acetate [S3]

^{1}H NMR: (500 MHz, $CDCl_3$)

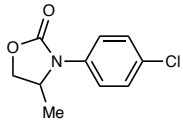
δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 5.5 Hz, 1H), 4.64 (dd, *J* = 10.8, 5.7 Hz, 1H), 4.35 (d, *J* = 10.8 Hz, 1H), 2.10 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.45, 154.70, 134.21, 132.04, 129.61, 123.23, 81.54, 68.58, 21.04

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{10}NO_4ClNa$ $[M+Na]^+$: 278.0196, found 278.0198.



3-(4-chlorophenyl)-4-methyloxazolidin-2-one [7]

^{1}H NMR: (500 MHz, $CDCl_3$)

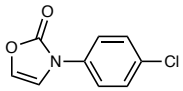
δ 7.36 (AB q, *J* = 9.0 Hz, 4H), 4.57 (t, *J* = 8.3 Hz, 1H), 4.53-4.44 (m, 1H), 4.02 (dd, *J* = 8.2, 5.7 Hz, 1H), 1.32 (d, *J* = 6.1 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 155.55, 135.30, 130.56, 129.36, 123.01, 68.75, 52.33, 18.45

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{10}H_{11}NO_2Cl$ $[M+H]^+$: 212.0478, found 212.0473.



3-(4-chlorophenyl)oxazol-2(3*H*)-one [S4]

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.53 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 2.2, 1H)

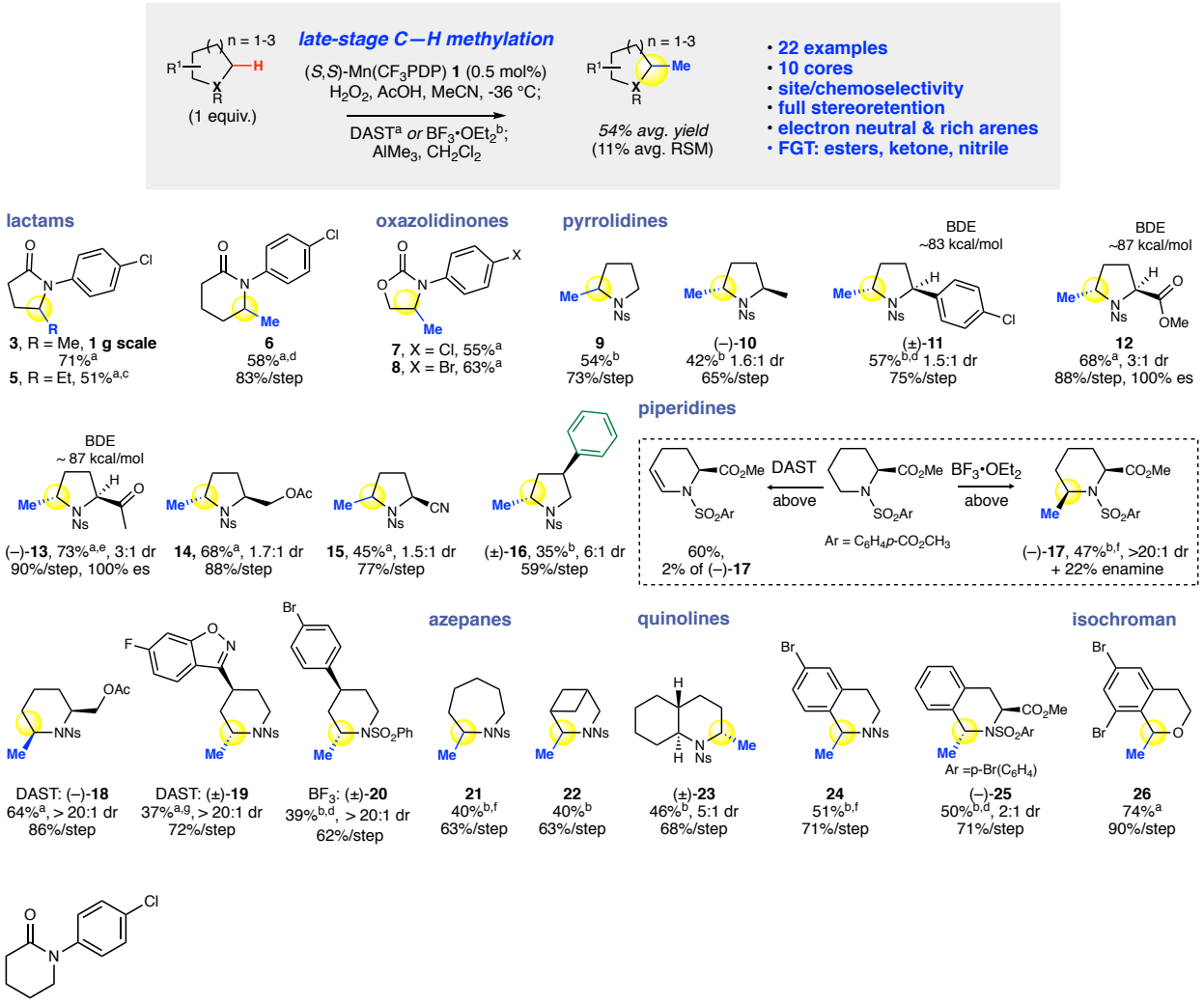
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 153.19, 134.16, 132.33, 129.77, 128.96, 122.26, 114.80

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_9H_7NO_2Cl$ $[M+H]^+$: 196.0165, found 196.0170.

III. Preparation and characterization of newly reported starting materials for Figure 3



1-(4-chlorophenyl)piperidin-2-one [S5] 4-chloroaniline (1.15 g, 9.00 mmol, 1 equiv.) was dissolved in DCM (20 mL) at 0 °C. 5-bromovaleryl chloride (1.2 mL, 9.0 mmol, 1 equiv.) was added dropwise, and a white precipitate was immediately formed. The reaction was stirred at room temperature for two hours, then diluted with brine (20 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The crude yield was 53%. The crude was then dissolved in THF (20 mL) under argon, and cooled to 0 °C. KO^{t}Bu (895 mg, 7.98 mmol, 1.01 equiv.) was then added slowly. The reaction was stirred at 0 °C for two hours before being quenched with brine (20 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (150 mL silica, loaded with DCM, gradient elution 300 mL 0% → 400 mL 10% → 20% → 30% → 40% → 1.5 L 50%

EtOAc/Hex) to afford 1-(4-chlorophenyl)piperidin-2-one as a white solid in 36% yield (670.4 mg, 3.2 mmol).

^{1}H NMR: (500 MHz, $CHCl_3$)

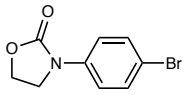
δ 7.34 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 3.61 (t, *J* = 5.5 Hz, 2H), 2.55 (t, *J* = 6.2 Hz, 2H), 1.98 – 1.88 (m, 4H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.35, 142.13, 132.45, 129.55, 127.81, 51.86, 33.16, 23.81, 21.72

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{13}ClNO$ $[M+H]^+$: 210.0686, found 210.0684



3-(4-bromophenyl)oxazolidin-2-one [S6] In a 100 mL recovery flask were added 2-oxazolidinone (523 mg, 6.0 mmol, 1.2 equiv.), 1-bromo-4-iodobenzene (1.41 g, 5.0 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 0.01 equiv.), XantPhos (86.8 mg, 0.15 mmol, 0.03 equiv.), and potassium phosphate (1.49 g, 7.0 mmol, 1.4 equiv.). A reflux condenser was placed on the flask, and the system was refilled with argon 3x. 1,4-dioxane (30 mL) was then added, and the mixture was refluxed in 100 °C oil bath overnight under nitrogen atmosphere. Upon completion, the reaction was diluted with CH_2Cl_2 and passed through a Celite plug. The resulting solution was condensed in vacuo and purification via flash chromatography yielded the product as a pale yellow crystalline solid, which was triturated with diethyl ether (3x5 mL) (1.03 g, 4.24 mmol, 85% yield).

^{1}H NMR: (500 MHz, $CHCl_3$)

δ 7.48 (d, *J* = 9.1 Hz, 2H), 7.43 (d, *J* = 9.1 Hz, 2H), 4.48 (dd, *J* = 8.7, 7.2 Hz, 2H), 4.03 (dd, *J* = 8.7, 7.3 Hz, 2H)

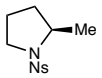
These data matched those reported in the literature[9].

General procedure for nosyl protection: In a 100 mL recovery flask at room temperature was added the amine (1.0 equiv.), 4-dimethylaminopyridine (DMAP) (0.1 equiv.), and methylene chloride (0.2 M). Triethylamine (Et_3N) (1.1 equiv.) was then added, followed by 4-nitrobenzenesulfonyl chloride (NsCl) (1.1 equiv.). The reaction was allowed to stir overnight, then quenched with saturated sodium bicarbonate solution. The layers were separated and the aqueous layer was extracted twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, condensed in vacuo, and purified through flash chromatography.

1-((4-nitrophenyl)sulfonyl)pyrrolidine [S7] According to the general procedure for nosyl protection, pyrrolidine (285 mg, 4.0 mmol, 1.0 equiv.) was reacted with DMAP (48.9 mg, 0.4 mmol, 0.1 equiv.), Et_3N (614 µL, 445 mg, 4.4 mmol, 1.1 equiv.), and NsCl (975 mg, 4.4 mmol, 1.1 equiv.) in CH_2Cl_2 (20 mL). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 20%→40%→60% EtOAc/Hex) to afford the product as a light yellow powder (1.00 g, 3.91 mmol, 98% yield). The NMR data matched those reported in the literature[10].

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 3.29 (ddd, *J* = 6.8, 4.4, 2.8 Hz, 4H), 1.86-1.76 (m, 4H)

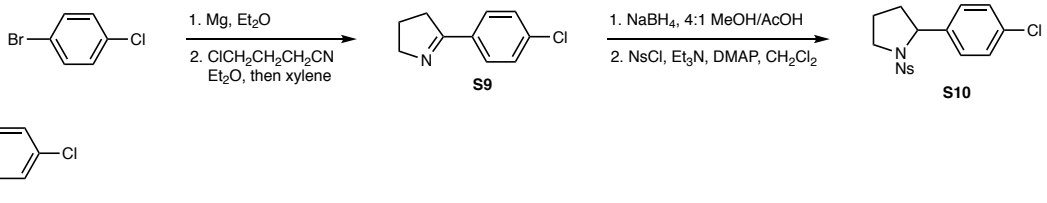


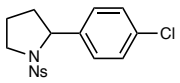
(*R*)-2-Methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine [S8] According to the general procedure for nosyl protection, (*R*)-2-methylpyrrolidine (250 mg, 2.94 mmol, 1.0 equiv.) was reacted with DMAP (35.7 mg, 0.294 mmol, 0.1 equiv.), Et_3N (451 µL, 327 mg, 3.23 mmol, 1.1 equiv.), and NsCl (717 mg, 3.23 mmol, 1.1 equiv.) in CH_2Cl_2 (14.7 mL). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→400 mL 20% EtOAc/Hex) to afford the product as a light yellow powder (653 mg, 2.41 mmol, 89% yield). The spectra data match with **12** (vide infra).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.37 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 3.78 (pd, *J* = 6.5, 4.2 Hz, 1H), 3.49 (ddd, *J* = 10.4, 7.1, 4.8 Hz, 1H), 3.19 (dt, *J* = 10.3, 7.4 Hz, 1H), 1.97-1.84 (m, 1H), 1.81-1.70 (m, 1H), 1.67-1.51 (m, 2H), 1.33 (d, *J* = 6.4 Hz, 3H)

$[\alpha]_D^{24}$ = -70.4º (c = 1.00, CH_2Cl_2)





2-(4-chlorophenyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine [S10] In a flame-dried 25-mL recovery flask equipped with a magnetic stir bar were added magnesium (304 mg, 12.5 mmol, 1 equiv.) and small

piece of iodine. Diethyl ether (1 mL) was then added to afford a brown solution. 1-Chloro-4-iodobenzene (2.4 g, 12.5 mmol, 1 equiv.) dissolved in Et_2O (1 mL) was then added dropwise. The reaction was allowed to stir at room temperature for 30 min. 4-chlorobutanenitrile (1.2 mL, 1.3 g, 12.5 mmol, 1 equiv.) was dissolved in Et_2O (1.2 mL) and added to the freshly prepared Grignard reagent. The resulting mixture was refluxed for 1 h; upon which diethyl ether was removed through distillation while xylene (12.5 mL) was added to the flask. The resulting mixture was then refluxed overnight. Upon completion, the reaction mixture was partitioned between ethyl acetate and NH_4Cl solution, and the aqueous layer extracted with EtOAc (2x10 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flash chromatography afforded 5-(4-chlorophenyl)-3,4-dihydro-2*H*-pyrrole **S9** as a yellow powder (922 mg, 5.13 mmol, 41% yield), ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.06 (dd, *J* = 7.5, 2.0 Hz, 2H), 2.97-2.87 (m, 2H), 2.10-2.00 (m, 2H). In a 100-mL recovery flask was added **S9** (922 mg, 5.13 mmol, 1 equiv.), MeOH (6.1 mL), and AcOH (1.5 mL). The reaction mixture was cooled to -36 °C, and sodium borohydride (433 mg, 11.4 mmol, 2.23 equiv.) was added slowly in one portion. The solution was then allowed to warm up to room temperature and stirred for 2 h. The solvents were removed in vacuo and water was added. The mixture was partitioned between 1 M NaOH and CH_2Cl_2, and the aqueous layer was extracted with CH_2Cl_2 (3x10 mL). The organic layers were combined, dried over K_2CO_3, and condensed in vacuo. According to the general procedure for nosyl protection, the crude was directly reacted with DMAP (62.7 mg, 0.513 mmol, 0.1 equiv.), Et_3N (787 µL, 571 mg, 5.64 mmol, 1.1 equiv.), and NsCl (1.25 g, 5.64 mmol, 1.1 equiv.) in CH_2Cl_2 (25 mL). Following workup, the crude material was purified by flash chromatography (75 mL silica, gradient elution 100 mL 0%→ 200 mL 10%→400 mL 50% EtOAc/Hex) to afford the product as a light yellow powder (787 mg, 2.15 mmol, 42% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

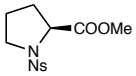
δ 8.31 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.81 (dd, *J* = 7.9, 4.1 Hz, 1H), 3.65 (ddd, *J* = 9.7, 6.9, 5.0 Hz, 1H), 3.53 (dt, *J* = 9.9, 7.0 Hz, 1H), 2.18-2.05 (m, 1H), 2.02-1.89 (m, 1H), 1.89-1.74 (m, 2H)

^{13}C NMR: (126 MHz, $CDCl_3$)

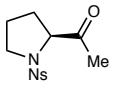
δ 150.10, 144.34, 140.70, 133.49, 128.76, 128.54, 127.79, 124.33, 63.25, 49.64, 36.08, 24.28

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{16}H_{16}ClN_2O_4S$ $[M+H]^+$: 367.0519, found 367.0524.



Methyl ((4-nitrophenyl)sulfonyl)-*L*-prolinate [S11] Synthesized using a previously reported synthesis and the NMR data matched those reported[5].



(*S*)-1-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)ethan-1-one [S12] In a 100-mL recovery flask containing *tert*-butyl (*S*)-2-acetylpyrrolidine-1-carboxylate[11] (1.05 g, 4.93 mmol, 1 equiv.) were added CH_2Cl_2 (10 mL) and trifluoroacetic acid (1.9 mL, 24.7 mmol, 5 equiv.). The mixture was stirred overnight, concentrated, redissolved in CH_2Cl_2 (10 mL), and washed with NaOH (1M, 5 mL). The aqueous layer was extracted with CH_2Cl_2 (3x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. According to the general procedure for nosyl protection, the crude was directly reacted with DMAP (60.2 mg, 0.493 mmol, 0.1 equiv.), Et_3N (756 µL, 548 mg, 5.42 mmol, 1.1 equiv.), and NsCl (1.20 g, 5.42 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL). Following workup, the crude material was purified thrice by flash chromatography (50 mL silica, 400 mL 40% EtOAc/Hex) to afford the product as a light yellow powder (203 mg, 0.68 mmol, 14% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 4.20 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.48 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.34 (dt, *J* = 9.7, 6.8 Hz, 1H), 2.26 (s, 3H), 2.06-1.95 (m, 1H), 1.95-1.79 (m, 2H), 1.78-1.64 (m, 1H)

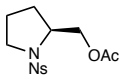
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 206.69, 150.39, 143.66, 128.96, 124.48, 67.65, 49.06, 29.82, 26.48, 24.90

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_6S$ $[M+H]^+$: 329.0807, found 329.0804.

$[\alpha]_D^{24}$ = -71.4º (c = 0.72, CH_2Cl_2)



(*S*)-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methyl acetate [S13] According to the general procedure for nosyl protection, L-prolinol (425 mg, 4.20 mmol, 1 equiv.) was reacted with DMAP (51.3 mg, 0.420 mmol, 0.1 equiv.), Et_3N (644 µL, 467 mg, 4.62 mmol, 1.1 equiv.), and NsCl (1.02 g, 4.62 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elusion 300 mL 30%→50% EtOAc/Hex) to afford (*S*)-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methanol as a mixture with byproducts (roughly 1.01 g, 3.53 mmol). The crude was transferred to a 100-mL recovery flask, where DMAP (43.1 mg, 0.353 mmol, 0.1 equiv.),

CH_2Cl_2 (7 mL), Et_3N (1.48 mL, 1.07 g, 10.6 mmol, 3 equiv.), and Ac_2O (1.67 mL, 1.80 g, 17.7 mmol, 5 equiv.) were added in order. The mixture was stirred overnight, and partitioned between saturated $NaHCO_3$ and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flash chromatography (50 mL silica, gradient elusion 200 mL 20%→30%→40% EtOAc/Hex) afforded the product as a white powder (1.14 g, 3.48 mmol, 83% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 4.21 (dd, *J* = 11.2, 4.9 Hz, 1H), 4.13 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.97-3.90 (m, 1H), 3.50 (ddd, *J* = 10.5, 7.2, 4.0 Hz, 1H), 3.24-3.17 (m, 1H), 2.07 (s, 3H), 1.98-1.86 (m, 1H), 1.82-1.74 (m, 1H), 1.72-1.62 (m, 2H)

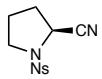
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.79, 150.33, 143.57, 128.80, 124.54, 65.89, 58.37, 49.44, 28.86, 24.18, 21.01

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_6S$ $[M+H]^+$: 329.0807, found 329.0804.

$[\alpha]_D^{24}$ = -87.5º (c = 0.99, CH_2Cl_2)



(*S*)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonitrile [S14] According to literature[12], in a 250-mL round-bottom flask were added ((4-nitrophenyl)sulfonyl)-*L*-proline[5] (4.53 g, 15.1 mmol, 1 equiv.), THF (20 mL), Et_3N (2.1 mL, 1.53 g, 15.1 mmol, 1 equiv.), and ethyl carbonochloridate (1.44 mL, 1.64 g, 15.1 mmol, 1 equiv.). The reaction mixture was stirred for 20 min, upon which NH_4OH (30 wt%, 1 mL, 17.6 mmol, 1.17 equiv.) was added. The reaction was then stirred overnight. Upon completion, the solvent was removed in vacuo and the crude redissolved in CH_2Cl_2. The organic layer was washed with sat. $NaHCO_3$ and isolated, dried over $MgSO_4$, and condensed in vacuo. THF (80 mL) and Et_3N (6.3 mL, 4.58 g, 45.3 mmol, 3 equiv.) were then added, followed by TFAA (3.2 mL, 4.76 g, 22.7 mmol, 1.5 equiv.). The reaction mixture was stirred for 3 h, and then quenched with water. The solvent was removed in vacuo and the residue redissolved in CH_2Cl_2, washed with 10% citric acid, brine, and sat. $NaHCO_3$. Purification by flash chromatography (50 mL silica, gradient elusion 200 mL 20%→40%→60%→80%→100% EtOAc/Hex) and recrystallization (80 mL methanol, 45 mL hexanes) afforded the product as a yellow crystalline solid (2.50 g, 8.89 mmol, 59% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 4.74 (dd, *J* = 6.2, 4.3 Hz, 1H), 3.56 (dd, *J* = 9.1, 7.7 Hz, 1H), 3.35 (ddd, *J* = 9.3, 6.9, 5.0 Hz, 1H), 2.35-2.23 (m, 2H), 2.19-2.07 (m, 2H)

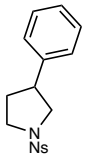
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.65, 143.56, 128.89, 124.69, 117.38, 48.80, 47.64, 32.04, 24.90

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{12}N_3O_4S$ $[M+H]^+$: 282.0549, found 282.0556.

$[\alpha]_D^{24}$ = -93.5º (c = 1.11, CH_2Cl_2)



1-((4-nitrophenyl)sulfonyl)-3-phenylpyrrolidine [S15] According to the general procedure for nosyl protection, 3-phenylpyrrolidine (294 mg, 2.00 mmol, 1.0 equiv.) was reacted with Et_3N (307 µL, 223 mg, 2.20 mmol, 1.1 equiv.), and NsCl (488 mg, 2.20 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL). Following workup, the crude material was purified by flash chromatography (50 mL silica, 200 mL 20% EtOAc/Hex) to afford the product as a yellow powder (613 mg, 1.84 mmol, 92% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

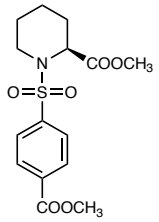
δ 8.39 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.34-7.19 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.78 (dt, *J* = 6.8, 2.0 Hz, 1H), 3.58 (ddd, *J* = 9.8, 8.8, 3.3 Hz, 1H), 3.46-3.38 (m, 1H), 3.35-3.27 (m, 1H), 3.26 (t, *J* = 7.7 Hz, 1H), 2.27 (ddd, *J* = 13.1, 6.7, 3.2 Hz, 1H), 1.96 (dq, *J* = 12.6, 9.1 Hz, 1H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.26, 143.25, 139.97, 128.92, 128.62, 127.38, 126.98, 124.54, 54.35, 48.07, 44.02, 32.86

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{16}H_{17}N_2O_4S$ $[M+H]^+$: 333.0909, found 333.0898.



Methyl (*S*)-1-((4-(methoxycarbonyl)phenyl)sulfonyl)piperidine-2-carboxylate [S16] *L*-Homoproline (258.32 mg, 2.0 mmol, 1 equiv.) was dissolved in dry MeOH (0.1M) under N_2 and cooled to 0 °C. $SOCl_2$ (1.0 mL, 14 mmol, 7 equiv.) was added dropwise. The ice bath was removed and the reaction was stirred at room temperature overnight. It was then azeotroped under vacuum with methanol. The resulting yellow solid was then dissolved in DCM (0.1M), and DMAP (24 mg, 0.2 mmol, 0.1 equiv.) and triethylamine

(613 µL, 4.4 mmol, 2.2 equiv.) were added respectively. Methyl 4-(chlorosulfonyl)benzoate (704 mg, 3 mmol, 1.5 equiv.) was added slowly and the resulting amber solution was stirred at room temperature overnight. The dark brown solution was then diluted with DCM and $NaHCO_3$, and the aqueous layer was extracted with DCM three times. The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography (75 mL silica, loaded with DCM, gradient elution 800 mL 20% EtOAc/Hex) to afford methyl (*S*)-1-((4-(methoxycarbonyl)phenyl)sulfonyl)piperidine-2-carboxylate as a yellow solid in 98% yield (666 mg, 1.95 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 4.74 (d, J = 4.4, 1H), 3.92 (s, 3H), 3.79 (d, J = 11.2 Hz, 1H), 3.49 (s, 3H), 3.16 (td, *J* = 12.8, 2.9 Hz, 1H), 2.11 (d, J = 10.8 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.68-1.60 (m, 2H), 1.46 (dddd, *J* = 17.8, 8.3, 7.1, 4.0 Hz, 1H), 1.23 (qt, J = 14.11, 3.70 Hz, 1H).

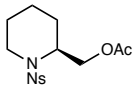
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 170.91, 165.77, 143.97, 133.58, 130.08, 127.19, 55.26, 52.64, 52.09, 42.89, 27.89, 24.80, 20.07.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{15}H_{19}NaNO_6S$ $[M+Na]^+$: 364.0831, found 364.0820.

$[\square]_D^{24}$ = -28.7 (c = 1.00, EtOH)



(*S*)-(1-((4-nitrophenyl)sulfonyl)piperidin-2-yl)methyl acetate [S17] (*S*)-piperidin-2-ylmethanol (760 mg, 6.6 mmol, 1 equiv.) was dissolved in DCM (0.1 M) at 0 °C. Triethylamine (966 µL, 6.93 mmol, 1.05) was added dropwise. Nosyl chloride (1.54 g, 6.92 mmol, 1.05 equiv.) was added portion-wise. The reaction was brought to RT and stirred overnight. It was then diluted with $NaHCO_3$ (15 mL), and the aqueous layer was extracted three times (3 x 10 mL). The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (100 mL silica, DCM loaded, gradient elution 300 mL 0% → 20% → 30% → 50% EtOAc/Hex) to afford the desired product as an oil in 37% yield (733 mg, 2.44 mmol). The resulting alcohol was dissolved in DCM (20 mL) and acetic anhydride (1.2 mL, 12.2 mmol, 5 equiv.) was added followed by triethylamine (690 µL, 4.88 mmol, 2 equiv.). The solution was stirred overnight at RT before being diluted with $NaHCO_3$ (15 mL). The aqueous layer was extracted three times (3 x 10 mL). The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting oil was purified by flash chromatography

(100 mL silica, DCM loaded, gradient elution 300 mL 0% → 10% → 20% → 30% EtOAc/Hex) to afford the desired product as white solid in 72% yield (600 mg, 1.75 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 2H), 4.41 – 4.26 (m, 2H), 4.08 (dd, *J* = 10.7, 5.3 Hz, 1H), 3.78 (dd, *J* = 14.5, 5.2 Hz, 1H), 3.12 (td, *J* = 13.9, 2.6 Hz, 1H), 2.02 (s, 3H), 1.69 – 1.64 (m, 1H), 1.62 – 1.55 (m, 2H), 1.53 – 1.43 (m, 2H), 1.31 – 1.17 (m, 1H).

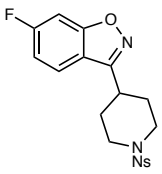
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 171.06, 150.17, 147.75, 128.41, 124.72, 61.38, 51.88, 41.75, 25.74, 24.89, 21.19, 19.09.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{14}H_{19}N_2O_6S$ $[M+H]^+$: 343.0964, found 343.0974.

$[\square]_D^{24}$ = -22.5 (c = 1.00, EtOH)



6-fluoro-3-(1-((4-nitrophenyl)sulfonyl)piperidin-4-yl)benzo[*d*]isoxazole [S18] 6-Fluoro-3-(4-piperidinyl)benzisoxazole hydrochloride (2.05 g, 8.00 mmol, 1 equiv.) was dissolved in DCM (15 mL, 0.5 M). DMAP (90 mg, 0.80 mmol, 0.1 equiv.), triethylamine (3.3 mL, 24 mmol, 3 equiv.) and nosyl chloride (3.5 g, 16 mmol, 2 equiv.) were added respectively. The solution was stirred for 12 hours before being diluted with 1 M NaOH (10 mL). The aqueous layer was extracted with DCM (3x15 mL), and the combined organics were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting brown oil was purified by flash chromatography (200 mL silica, DCM loaded, gradient elution 200 mL 0% → 300 mL 15% → 20% → 30% → 40% EtOAc/Hex → 1.6 L EtOAc) to afford the desired product as a yellow powder in 77% yield (2.50 g, 6.17 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.41 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.57 (dd, *J* = 8.7, 5.0 Hz, 1H), 7.25 (dd, *J* = 5.2, 1.6 Hz 1H), 7.07 (td, *J* = 8.8, 2.2 Hz, 1H), 3.88 (dt, *J* = 11.9, 3.8 Hz, 2H), 3.12 (tt, *J* = 9.8, 5.1 Hz, 1H), 2.73 (ddd, *J* = 12.1, 9.6, 4.2 Hz, 2H), 2.34 – 2.07 (m, 4H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

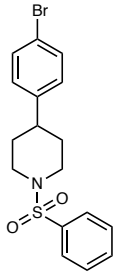
δ 164.36 (d, *J* = 251.7 Hz), 164.10 (d, *J* = 13.6 Hz), 159.71, 150.40, 142.65, 128.91, 124.58, 122.13 (d, *J* = 11.1 Hz), 116.98, 112.94 (d, *J* = 25.1 Hz), 97.81 (d, *J* = 26.8 Hz), 45.86, 33.22, 29.68

^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -108.69 (td, *J* = 8.6, 5.1 Hz)

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{18}H_{17}FN_3O_5S$ $[M+H]^+$: 406.0873; found 406.0870.



4-(4-bromophenyl)-1-(phenylsulfonyl)piperidine [S19] 4-(4-bromophenyl)piperidine•HCl (304.3mg, 1.100 mmol, 1.0 equiv.) was dissolved in DCM (5 mL, 0.2 M) at rt. DMAP (13.4 mg, 0.110 mmol, 0.1 equiv.), triethylamine (337 µL, 2.42 mmol, 2.20 equiv.) and benzenesulfonyl chloride (281 µL, 2.20 mmol, 2.00 equiv.) were added respectively. The solution was stirred for 12 hours and then diluted with sat. $NaHCO_3$ (10 mL). The aqueous layer was extracted three times with DCM (3x10 mL), and the combined organics were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography (75 mL silica, DCM loaded, gradient elution 200 mL 0% → 7.5% → 10% → 12% EtOAc/Hex) to afford the desired product as a lightly yellow powder in 83% yield (347 mg, .913 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 3.95 (d, *J* = 11.7 Hz, 2H), 2.43-2.33 (m, 3H), 1.91 – 1.71 (m, 4H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 143.92, 136.39, 132.88, 131.80, 129.17, 128.56, 127.81, 120.42, 46.84, 41.45, 32.57.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{17}H_{19}BrNO_2S$ $[M+H]^+$: 380.0320, found 380.0309.

1-((4-nitrophenyl)sulfonyl)azepane [S20] Azepane (451 µL, 4 mmol, 1.0 equiv.) was dissolved in DCM (0.4 M). DMAP (49mg, 0.4 mmol, 0.1 equiv.), NEt_3 (1.1 mL, 8 mmol, 2 equiv.) and nosyl chloride (1.77 g, 8 mmol, 2 equiv.) were added respectively and stirred at room temperature overnight. The resulting brown solution was diluted with $NaHCO_3$ (15 mL), and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The resulting

oil was purified by column chromatography (100 mL silica, DCM loaded, 200 mL 0% → 300 mL 5% → 10% → 20% → 600 mL 50% ethyl acetate in hexanes) to afford 1-((4-nitrophenyl)sulfonyl)azepane as a white powder in 99% yield (1.13 g, 3.96 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 3.31 (d, *J* = 4.8 Hz, 4H), 1.78-1.68 (m, 4H), 1.65-1.56 (m, 4H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 149.96, 145.65, 128.17, 124.46, 48.55, 29.29, 26.97.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{12}H_{17}N_2O_4S$ $[M+H]^+$: 285.0909, found 285.0912.

3-((4-nitrophenyl)sulfonyl)-3-azabicyclo[3.1.1]heptane [S21] 3-azabicyclo[3.1.1]heptane•HCl (270 mg, 2 mmol, 1 equiv.) was dissolved in DCM (0.4 M). NEt_3 (836µL, 6 mmol, 3 equiv.) and nosyl chloride (886 mg, 4 mmol, 2 equiv.) were added respectively and stirred at room temperature overnight. The resulting brown solution was diluted with DCM (20 mL) and $NaHCO_3$ (15 mL), and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (100 mL silica, DCM loaded, 200 mL 0% → 300 mL 10% → 20% → 20% ethyl acetate in hexanes) to afford 3-((4-nitrophenyl)sulfonyl)-3-azabicyclo[3.1.1]heptane as a pale yellow powder in 98% yield (558 mg, 1.96 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

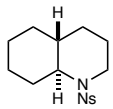
δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 3.56 (s, 4H), 2.44 (tt, *J* = 6.3, 1.4 Hz, 2H), 2.10 (qt, *J* = 7.8, 3.9 Hz, 2H), 1.17 (dt, *J* = 7.9, 3.9 Hz, 2H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 150.31, 143.87, 128.69, 124.64, 51.56, 32.34, 31.42.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{12}H_{15}N_2O_4S$ $[M+H]^+$: 283.0753, found 283.0757.



trans-1-((4-nitrophenyl)sulfonyl)decahydroquinoline [(±)-S22] *Trans*-decahydroquinoline (696 mg, 5 mmol, 1 equiv.) was dissolved in DCM (15 mL, 0.33M). Triethylamine (1.05 mL, 7.50 mmol, 1.5 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.) and nosyl chloride (2.2 g, 10 mmol, 2 equiv.) were added respectively. The solution was stirred for 12 hours, and the resulting brown solution was quenched with $NaHCO_3$ (10 mL). The aqueous layer was extracted with DCM (3 x 10 mL), and the organic layers were combined, dried with Na_2SO_3, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (200 mL silica, DCM loaded, gradient elution 200 mL 0% → 400 mL 10% → 15% → 15% EtOAc/Hex) to afford the desired product as a white powder in 83% yield (1.35 g, 4.16 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

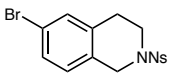
δ 8.34 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 4.13 (dtd, *J* = 12.9, 4.3, 1.4 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.65 (dt, *J* = 8.7, 2.8 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.80-1.58 (m, 7H), 1.54 – 1.41 (m, 1H), 1.29 – 1.09 (m, 2H), 1.08 – 0.88 (m, 2H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 149.88, 147.61, 128.32, 124.39, 65.70, 48.84, 41.02, 33.48, 31.69, 31.59, 26.06, 25.54, 25.41.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$: 325.1222, found 325.1227.



6-bromo-2-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline [S23] 6-Bromo-1,2,3,4-tetrahydroisoquinoline hydrochloride (373 mg, 1.50 mmol, 1 equiv.) was dissolved in DCM (5 mL, 0.3M). DMAP (18 mg, 0.15, 0.1 equiv.), triethylamine (627 µL, 4.50 mmol, 3 equiv.) and nosyl chloride (665 mg, 3.00 mmol, 2 equiv.) were added respectively. The solution was stirred for 12 hours before being diluted with sat. $NaHCO_3$ (10 mL). The aqueous layer was extracted with DCM (3x10 mL), and the combined organic layers were dried with Na_2CO_3 and concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography (100 mL silica, DCM loaded, gradient elution 200 mL 0% → 300 mL 15% → 25% → 60% EtOAc/Hex) to afford the desired product as a pale yellow solid in 81% yield (486.6 mg, 1.22 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

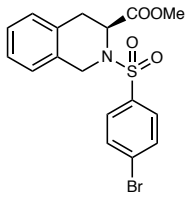
δ 8.38 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 4.29 (s, 2H), 3.45 (t, *J* = 5.9 Hz, 2H), 2.91 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 150.40, 142.99, 135.11, 131.93, 130.07, 129.95, 128.85, 128.01, 124.59, 120.95, 47.17, 43.48, 28.62.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{15}H_{14}BrN_2O_4S$ $[M+H]^+$: 396.9858, found 396.9710.



(methyl (*S*)-2-((4-bromophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate [S24] (*S*)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid (532 mg, 3 mmol, 1equiv.) was dissolved in dry MeOH (0.1 M) under N_2 and cooled to 0 °C. $SOCl_2$ (1.5 mL, 21 mmol, 7 equiv.) was added dropwise. The ice bath was removed and the reaction was stirred at room temperature overnight. It was then azeotroped under vacuum with methanol. The resulting yellow solid was then dissolved in DCM (0.1 M), and DMAP (37 mg, 0.3 mmol, 0.1 equiv.) and triethylamine (1.25 mL, 9 mmol, 3 equiv.) were added respectively. 4-bromo-benzenesulfonyl chloride (1.53g, 6 mmol, 2 equiv.) was added slowly and the resulting yellow solution was stirred at room temperature overnight. The dark brown solution was then diluted $NaHCO_3$ (20 mL), and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting brown oil was purified with column chromatography (100 mL silica, loaded with DCM, 150 mL 0% → 300 mL 10% → 15% → 25% ethyl acetate in hexanes) to afford methyl (methyl (*S*)-2-((4-bromophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate as a yellow oil in 90% yield (1.1g, 2.7 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.16 (tt, *J* = 7.3, 5.6 Hz, 2H), 7.09 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.6 Hz, 1H), 5.01 (t, *J* = 4.6 Hz, 1H), 4.71 (d, *J* = 15.3 Hz, 1H), 4.47 (d, *J* = 15.4 Hz, 1H), 3.47 (s, 3H), 3.21 (d, *J* = 4.5 Hz, 2H).

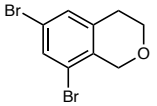
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 170.62, 138.19, 132.32, 131.22, 130.69, 129.03, 128.95, 127.86, 127.14, 127.08, 126.26, 54.09, 52.48, 44.58, 32.04.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{17}H_{17}BrNO_4S$ $[M+H]^+$: 410.0062, found 409.9981

$[\alpha]_D^{24}$ = -15.4 (c = 1.00, EtOH)



6,8-dibromoisochromane [S25] 3,5-dibromo-benzeneacetic acid (1.18 g, 4.01 mmol, 1 equiv.) was dissolved in THF (20 mL) under argon at 0 °C. BH_3•THF (2M solution, 8 mL, 8 mmol, 2 equiv.) was added dropwise. The ice bath was removed and the reaction stirred for 4 hours before being quenched with brine (15 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The resulting oil was dissolved in DCM (20 mL) and DIPEA (2.1 mL, 12 mmol, 3 equiv.) was added dropwise. MEMCl (913 µL, 8 mmol, 2 equiv.) was added dropwise. The solution was stirred overnight before being diluted with $NaHCO_3$ (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL), dried with Na_2SO_4, and concentrated *in vacuo*. The resulting oil was purified by column chromatography (150 mL silica, DCM loaded, 400 mL 0% → 10% → 15% → 20% ethyl acetate in hexanes) to afford 1,3-dibromo-5-(2-((2-methoxyethoxy)methoxy)ethyl)benzene as an oil in 61% yield (900 mg, 2.44 mmol). The MEM protected alcohol was dissolved in DCM (20 mL) under argon at 0 °C. $TiCl_4$ (439 µL, 4 mmol, 2 equiv.) was added dropwise at 0 °C and the reaction was stirred for 5 hours at 0 °C. It was diluted with $NaHCO_3$ (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL), and the combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (75 mL silica, loaded with 10% EtOAc/Hexanes, 300 mL 0% → 5% → 10% ethyl acetate in hexanes) to afford the desired isochroman in 74% yield as a white powder (531 mg, 1.81 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.53 (s, 1H), 7.24 (s, 1H), 4.63 (s, 2H), 3.90 (t, J = 5.6 Hz, 2H), 2.82 (t, J = 5.6 Hz, 2H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 138.15, 133.50, 132.69, 131.20, 121.56, 120.48, 68.70, 64.83, 28.45.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_9H_9Br_2O$ $[M+H]^+$: 290.9020, found 290.8856.

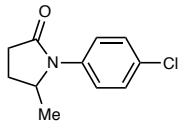
IV. Experimental procedures and compound characterization for Figure 3

General procedure for C–H oxidation: To a 40 mL vial equipped with a stir bar were added the substrate (0.30 mmol, 1.0 equiv,), (*S*,*S*)-Mn(CF_3PDP) **1** (2.0 mg, 0.0015 mmol, 0.005 equiv.), MeCN (0.6 mL, 0.5 M), and AcOH (257 μL, 4.50 mmol, 15.0 equiv.). For achiral or racemic substrates, (*R*,*R*)- and (*S*,*S*)-**1** can be used interchangeably. The reaction mixture was then placed into a -36 °C dry ice/1,2-dichloroethane bath. A 10 mL syringe was charged with a solution of H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). The syringe was then fitted with a 25G needle and the solution was slowly added into the stirring reaction mixture via a syringe pump at 3.75 mL/h. Upon completion, the vial was taken from the cold bath, and the reaction mixture was immediately loaded onto a 15 mL silica plug. Ethyl acetate was used to rinse the vial (2x1 mL), and the resulting washes were also loaded onto the silica plug. The plug was allowed to sit for five minutes in order to decompose any remaining hydrogen peroxide as well as absorbing the reaction mixture. Ethyl acetate (150 mL) was then allowed to pass through the plug, and the eluent was concentrated in vacuo, transferred into a 25 mL recovery flask, condensed and placed on vacuum overnight to remove the residual acetic acid.

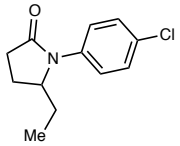
General procedure for BF_3-promoted methylation: The crude from oxidation was dissolved in CH_2Cl_2 (1.5 mL, 0.2 M), backfilled with nitrogen 3x, and placed into a -78 °C dry ice/acetone bath. Trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was then added dropwise, followed by boron trifluoride diethyl etherate (74.0 μL, 0.60 mmol, 2.0 equiv.). The reaction mixture was stirred at -78 °C for 1 h, then allowed to warm to room temperature while stirring for 3 h. Upon completion, the reaction was diluted with CH_2Cl_2 (5 mL) and poured into a 60 mL separatory funnel containing 3 mL 1 M NaOH for quenching. The aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and condensed in vacuo before subjecting to purification via flash or medium pressure chromatography.

General procedure for DAST-promoted methylation: The crude from oxidation was dissolved in CH_2Cl_2 (1.5 mL, 0.2 M), backfilled with nitrogen 3x, and placed into a -78 °C dry ice/acetone bath. Diethylaminosulfur trifluoride (39.6 μL, 48.3 mg, 0.30 mmol, 1.0 equiv.) or Deoxo-Fluor (55.3 μL, 66.4 mg, 0.30 mmol, 1.0 equiv.) was added, and the reaction was allowed to warm to room temperature while stirring for 1 h. The reaction was then placed back into -78 °C cold bath, where trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was then added dropwise. The reaction mixture was stirred at -78 °C for 2 h, then allowed to warm to room temperature while stirring for 1 h. Upon completion, the reaction was diluted with CH_2Cl_2 (5 mL) and poured into a 60 mL separatory funnel containing 3 mL 1 M NaOH for quenching. The aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were

combined, dried over anhydrous $MgSO_4$, filtered, and condensed in vacuo before subjecting to purification via flash or medium pressure chromatography.



1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one [3] Gram scale: Following the general oxidation and DAST-promoted procedures, 1-(4-chlorophenyl)pyrrolidin-2-one **2** (1.0 g, 5.11 mmol, 1.0 equiv.) in MeCN (10.2 mL) in a 100 mL round-bottom flask was oxidized with (*S*,*S*)-Mn(CF_3PDP) (34.6 mg, 0.0256 mmol, 0.005 equiv.), acetic acid (4.38 mL, 76.7 mmol, 15.0 equiv.), and H_2O_2 (581 µL, 10.2 mmol, 2.0 equiv., 50 wt.% in H_2O) in MeCN (60 mL, in 50 mL HSW syringe). Following oxidation, the solution was passed through 100 mL silica and flushed with 1 L of EtOAc. The solution was concentrated *in vacuo* and transferred to a 100 mL round bottom flask and left on a high vacuum pump overnight. The crude was then dissolved in 25.6 mL of CH_2Cl_2 under nitrogen and placed in a dry ice/acetone cold bath. DAST (675 µL, 5.11 mmol, 1.0 equiv.) was added and the solution was stirred for an hour. $AlMe_3$ (7.67 mL, 15.3 mmol, 3.0 equiv.) was then added slowly. The reaction was stirred at -78°C for two hours before removing the dry ice bath and stirring at rt for an additional hour. A 3 M solution of sodium hydroxide (100 mL) was cooled to 0 °C at the end of the reaction and transferred to a 250 mL separatory funnel. The reaction mixture was cooled to 0 °C and slowly transferred to the separatory funnel. The organic layer was carefully extracted, and the aqueous layer was washed with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried with $MgSO_4$, concentrated *in vacuo*, and purified via MPLC (40 g silica, 80 column volumes 0%→30% EtOAC/Hex) to afford the desired product as a light orange gel (764.6 mg, 3.647 mmol, 71% yield; 112.3 mg, 0.574 mmol, 11% rsm). See Table 1 for product characterization.



1-(4-chlorophenyl)-5-ethylpyrrolidin-2-one [5] Following the general oxidation and a modified DAST-promoted methylation procedures, 1-(4-chlorophenyl)pyrrolidin-2-one **2** (59.3 mg, 0.302 mmol, 1.00 equiv.) in MeCN (0.7 mL) was oxidized with (S,S)MnCF_3PDP (2.0 mg, 0.0015 mmol, 0.005 equiv.), acetic acid (259 µL, 4.53 mmol, 15.0 equiv.), and H_2O_2 (34 µL, 0.604 mmol, 2 equiv., 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M) at -36 °C via single addition protocol . Following oxidation, the crude was subjected to DAST (40 µL, 0.302 mmol, 1 equiv.) at -78°C and stirred at RT for 1 hour. After 1 hour, the

solution was brought to -78°C, and triethylaluminum (1.0 M in hexanes, 910 µL, 0.906 mmol, 3 equiv.) was added. The solution was stirred at -78°C for three hours before being quenched. Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 45 CV 0% to 20%, 10 CV 20% EtOAc/Hex) to produce the desired compound as a white powder.

Run 1 (33.8 mg, 0.151 mmol, 50% yield; 12% rsm by ^{1}H NMR)

Run 2 (33.1 mg, 0.148 mmol, 49% yield; 10% rsm by ^{1}H NMR)

Run 3 (37.3 mg, 0.167 mmol, 55% yield; 13% rsm by ^{1}H NMR)

Average overall yield: 51% (12% rsm) ± 2.6

^{1}H NMR: (500 MHz, $CDCl_3$)

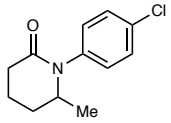
δ 7.36 (m, 4H), 4.16 (tdd, *J* = 8.2, 5.0, 3.0 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.60 – 2.51 (m, 1H), 2.33 (m, 1H), 1.91 – 1.82 (m, 1H), 1.76 – 1.65 (m, 1H), 1.44 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 174.51, 136.42, 131.11, 129.23, 125.23, 60.77, 31.42, 26.07, 23.31, 8.78

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{12}H_{15}ClNO$ $[M+H]^+$: 224.0842, found 224.0839.



1-(4-chlorophenyl)-6-methylpiperidin-2-one [6] Following the general oxidation and DAST-promoted methylation, 1-(4-chlorophenyl)piperidin-2-one **S5** (63.3 mg, 0.302 mmol, 1.00 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (S,S)-$MnCF_3$PDP (8.2 mg, 0.00604 mmol, 0.02 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (34 µL, 0.604 mmol, 2 equiv.) in MeCN (3.75 mL), at -36 °C via the single addition protocol. Following oxidation, the crude was subjected to DAST (40 µL, 0.303 mmol, 1.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 40% → 50% → 400 mL 60% EtOAc/Hex) to afford the desired product as a pale yellow oil in an average of 58% yield.

Run 1 (41.1 mg, 0.184 mmol, 61% yield; 5% rsm by ^{1}H NMR)

Run 2 (38.5 mg, 0.172 mmol, 57% yield; 5% rsm by ^{1}H NMR)

Run 3 (37.2 mg, 0.166 mmol, 55% yield; 4% rsm by ^{1}H NMR)

Average overall yield: 58% (5% rsm) ± 2.5

^{1}H NMR: (500 MHz, $CDCl_3$)

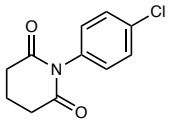
δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.89 (sxt, *J* = 6.3 Hz, 1H), 2.52 (t, *J* = 6.6 Hz, 2H), 2.14 – 2.06 (m, 1H), 2.03 – 1.93 (m, 1H), 1.89 – 1.79 (m, 1H), 1.72 (dddd, *J* = 13.3, 8.8, 6.2, 3.0 Hz, 1H), 1.06 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

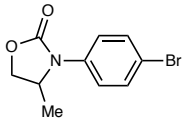
δ 170.70, 140.33, 133.05, 129.76, 129.65, 56.07, 33.07, 31.15, 21.22, 18.64

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{12}H_{15}ClNO$ $[M+H]^+$: 224.0842, found 224.0845.



Oxidation of **6** using 10 mol% **1** and 5 equiv. H_2O_2: 40.5 mg, 0.181 mmol, 60% imide; 4.1 mg, 0.151 mmol, 5% hemiaminal acetate; 6.8 mg, 0.0302 mmol, 10% hemiaminal, 5.0 mg, 0.0242 mmol, 8% olefin. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 2.82 (t, *J* = 6.5 Hz, 4H), 2.10 (p, *J* = 6.5 Hz, 2H).



3-(4-bromophenyl)-4-methyloxazolidin-2-one [8] According to a modified general oxidation and DAST-promoted methylation procedures, 3-(4-bromophenyl)oxazolidin-2-one **S6** (72.6 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.8 mL, 0.375 M) was placed in ice bath and oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (34.6 µL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with DAST (39.6 µL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→200 mL 20%→400 mL 30% EtOAc/Hex) to afford the product as a white powder.

Run 1 (48.6 mg, 0.190 mmol, 63% yield)

Run 2 (49.6 mg, 0.194 mmol, 65% yield)

Run 3 (46.2 mg, 0.180 mmol, 60% yield)

Average overall yield: 63% (0% rsm) ± 2.5

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.50 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 4.57 (t, *J* = 8.3 Hz, 1H), 4.53-4.44 (m, 1H), 4.02 (dd, *J* = 8.3, 5.5 Hz, 1H), 1.33 (d, *J* = 6.1 Hz, 3H)

The spectral data match with those reported in the literature[13].

2-Methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine [9] According to the general oxidation and BF_3-promoted methylation procedures, 1-((4-nitrophenyl)sulfonyl)pyrrolidine **S7** (76.9 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 μL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (34.6 μL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) and BF_3•OEt_2 (74.0 μL, 0.60 mmol, 2.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→400 mL 20% EtOAc/Hex) to afford the product as a white solid.

Run 1 (39.9 mg, 0.147 mmol, 49% yield; 4.6 mg, 0.018 mmol, 6% rsm; 20% 2,5-dimethylation by ^{1}H NMR, 1.4:1 dr)

Run 2 (43.9 mg, 0.162 mmol, 54% yield, 6.0 mg, 0.023 mmol, 8% rsm; 10% 2,5-dimethylation by ^{1}H NMR, 1.3:1 dr)

Run 3 (48.5 mg, 0.179 mmol, 60% yield, 9.6 mg, 0.037 mmol, 12% rsm; 14% 2,5-dimethylation by ^{1}H NMR, 1.3:1 dr)

Average overall yield: 54% (9% rsm) ± 5.5; 15% 2,5-dimethylation, 1.3:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

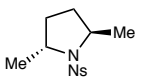
δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 3.76 (pd, *J* = 6.5, 3.8 Hz, 1H), 3.49 (ddd, *J* = 10.0, 7.0, 4.8 Hz, 1H), 3.17 (dt, *J* = 10.0, 7.2 Hz, 1H), 1.96-1.82 (m, 1H), 1.81-1.67 (m, 1H), 1.67-1.50 (m, 2H), 1.32 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.09, 144.14, 128.58, 124.40, 56.71, 49.19, 33.64, 24.06, 22.75

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{15}N_2O_4S$ $[M+H]^+$: 271.0753, found 271.0751.



(2*R*,5*R*)-2,5-dimethyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine [10] According to the general oxidation and BF_3-promoted methylation procedures, (*R*)-2-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine **S8** (81.1

mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (34.6 µL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.) and BF_3•OEt_2 (74.0 µL, 0.60 mmol, 2.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 5%→600 mL 20% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**. The ^{1}H NMR data matched those synthesized via an alternate route as reported by literature[14].

Run 1 (39.1 mg, 0.138 mmol, 46% yield, 1.4:1 dr; 11.0 mg, 0.041 mmol, 14% rsm)

Run 2 (35.0 mg, 0.123 mmol, 41% yield, 2:1 dr; 13.5 mg, 0.050 mmol, 17% rsm)

Run 3 (33.5 mg, 0.118 mmol, 39% yield, 1.4:1 dr; 10.7 mg, 0.040 mmol, 13% rsm)

Average overall yield: 42% (15% rsm) ± 3.6, 1.6:1 dr

Characterization of major diastereomer **10**:

^{1}H NMR: (400 MHz, $CDCl_3$)

δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 4.08 (app p, *J* = 6.5 Hz, 2H), 2.21-2.08 (m, 2H), 1.63-1.52 (m, 2H), 1.21 (d, *J* = 6.4 Hz, 6H)

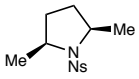
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 149.76, 148.69, 128.17, 124.33, 56.99, 31.30, 21.57

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{12}H_{17}N_2O_4S$ $[M+H]^+$: 285.0909, found 285.0911.

$[\alpha]_D^{24}$ = -21.6º (c = 0.21, CH_2Cl_2)



Characterization of minor diastereomer **S26**:

^{1}H NMR: (400 MHz, $CDCl_3$)

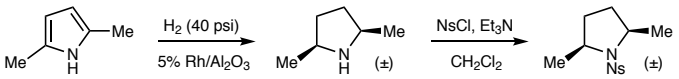
δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 3.80-3.58 (m, 2H), 1.70-1.52 (m, 4H), 1.37 (d, *J* = 6.3 Hz, 6H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.10, 144.34, 128.69, 124.37, 58.15, 32.30, 23.74

HRMS: (ESI-TOF MS ES+)

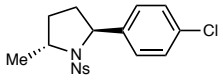
m/z calculated for $C_{12}H_{17}N_2O_4S$ $[M+H]^+$: 285.0909, found 285.0916.



Synthesis of the reference compound: According to literature[14], in a 25 mL recovery flask equipped with a magnetic stir bar were added 2,5-dimethylpyrrole (200 mg, 2.1 mmol, 1.0 equiv.), 5% rhodium on alumina (14.3 mg), and acetic acid (714 µL). The flask was placed into a bomb, backfilled with hydrogen 3x, and pressurized with hydrogen to 40 psi. The reaction was stirred for 3 d. Upon completion, the reaction mixture as diluted with CH_2Cl_2, and rhodium was removed via filtration. The filtrate was basified with 3 M NaOH and extracted with CH_2Cl_2 3x. The combined organic layer was dried over K_2CO_3, filtered, and carefully condensed in vacuo. Crude NMR of the resulting free amine shows a 3:1 syn/anti diastereomeric ratio. The ^{1}H NMR data of the anti-isomer matched those reported in the literature[15]. The crude was dissolved in CH_2Cl_2 (20 mL), where NsCl (512 mg, 2.31 mmol, 1.1 equiv.) and Et_3N (322 µL, 2.31 mmol, 1.1 equiv.) were added and the reaction was stirred overnight. Upon completion, the reaction mixture was washed with sat. $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 2x. The combined organic layer was dried over $MgSO_4$, filtered, and condensed in vacuo. Purification by medium-pressure liquid chromatography (12 g silica, 100 column volumes 0%→25% EtOAc/Hex) afforded nosyl 2,5-dimethylpyrrolidine as a mixture of diastereomers (193 mg, 0.680 mmol, 32% yield, 3:1 dr).

^{1}H NMR: (400 MHz, $CDCl_3$)

δ 8.36 (d, *J* = 8.8 Hz, 1.54H), 8.32 (d, *J* = 8.8 Hz, 0.46H), 8.08-7.96 (m, 2H), 4.07 (p, *J* = 6.4 Hz, 0.46H), 3.78-3.62 (m, 1.54H), 2.21-2.07 (m, 0.46H), 1.70-1.49 (m, 3.54H), 1.36 (d, *J* = 6.4 Hz, 2.31H), 1.20 (d, *J* = 6.4 Hz, 0.69H)



trans-2-(4-chlorophenyl)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine [(±)-11] According to the general oxidation and BF_3-promoted methylation procedures, 2-(4-chlorophenyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine **S10** (73.4 mg, 0.20 mmol, 1.0 equiv.) in MeCN (0.4 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (5.4 mg, 0.006 mmol, 0.02 equiv.), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (57.7 µL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M). Following oxidation, the crude was methylated with trimethylaluminum (2.0 M in hexanes, 300 µL, 0.60 mmol, 3.0 equiv.) and BF_3•OEt_2 (49.3 µL, 0.40 mmol, 2.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 5%→10%→20% EtOAc/Hex) to afford the product as a white powder as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**.

Run 1 (40.2 mg, 0.106 mmol, 53% yield, 1.3:1 dr; 8% rsm by ^{1}H NMR)

Run 2 (45.8 mg, 0.120 mmol, 60% yield, 1.4:1 dr; 6% rsm by ^{1}H NMR)

Run 3 (43.1 mg, 0.113 mmol, 57% yield, 1.7:1 dr; 6% rsm by ^{1}H NMR)

Average overall yield: 57% (7% rsm) ± 3.5, 1.5:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

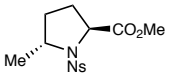
δ 8.31 (d, *J* = 8.8 Hz, 0.74H), 8.12 (d, *J* = 8.8 Hz, 1.26H), 7.90 (d, *J* = 8.8 Hz, 0.74H), 7.62 (d, *J* = 8.9 Hz, 1.26H), 7.27 (d, *J* = 9.1 Hz, 0.74H), 7.24 (d, *J* = 8.6 Hz, 0.74H), 7.08 (d, *J* = 8.4 Hz, 1.26H), 6.93 (d, *J* = 8.5 Hz, 1.26H), 4.97 (d, *J* = 8.4 Hz, 0.63H), 4.72 (t, *J* = 6.7 Hz, 0.37H), 4.34 (p, *J* = 6.5 Hz, 0.63H), 4.03 (sxt, *J* = 6.4 Hz, 0.37H), 2.53 (tdd, *J* = 12.9, 8.9, 7.1 Hz, 0.63H), 2.29 (tt, *J* = 12.8, 7.5 Hz, 0.63H), 2.03-1.96 (m, 0.37H), 1.93-1.85 (m, 0.37H), 1.85-1.74 (m, 1H), 1.70 (ddt, *J* = 12.7, 7.1, 1.3 Hz, 0.63H), 1.59 (dd, *J* = 11.8, 5.9 Hz, 0.37 H), 1.48 (d, *J* = 6.4 Hz, 1.11H), 1.43 (d, *J* = 6.4 Hz, 1.89H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.12, 149.52, 147.47, 144.37, 140.39, 140.27, 133.35, 133.43, 128.78, 128.77, 128.50, 128.34, 128.10, 127.91, 124.30, 123.82, 64.91, 63.27, 58.37, 58.34, 34.67, 33.16, 32.28, 31.85, 22.75, 22.12

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{18}N_2O_4SCl$ $[M+H]^+$: 381.0676, found 381.0683.



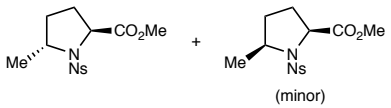
methyl (2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxylate [12] According to the general oxidation and DAST-promoted methylation procedures, methyl ((4-nitrophenyl)sulfonyl)-*L*-prolinate **S11** (94.2 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 μL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with DAST (39.6 μL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→400 mL 20% EtOAc/Hex) to afford the product as a white solid or gel as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42** and by converting the product to methyl 1-((4-fluorophenyl)sulfonyl)-5-methylpyrrolidine-2-carboxylate and comparing the ^{1}H NMR spectra to those reported in the literature[16].

Run 1 (71.9 mg, 0.219 mmol, 73% yield; 3:1 dr; 19% rsm by ^{1}H NMR)

Run 2 (61.1 mg, 0.186 mmol, 62% yield, 2:1 dr; 16% rsm by ^{1}H NMR)

Run 3 (68.2 mg, 0.208 mmol, 69% yield, 3:1 dr; 13% rsm by ^{1}H NMR)

Average overall yield: 68% (16% rsm) ± 5.6, 3:1 dr



^{1}H NMR: (500 MHz, $CDCl_3$)

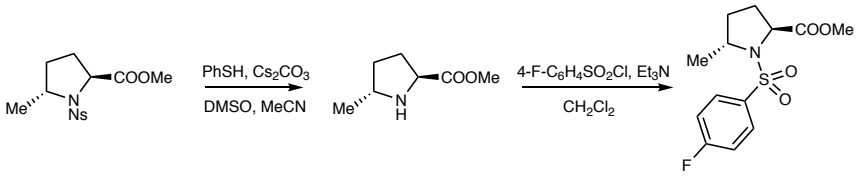
δ 8.36 (d, *J* = 9.1 Hz, 0.5H), 8.33 (d, *J* = 8.8 Hz, 1.5H), 8.10 (d, *J* = 8.7 Hz, 0.5H), 8.04 (d, *J* = 9.0 Hz, 1.5H), 4.51 (dd, *J* = 8.6, 1.3 Hz, 0.75H), 4.39 (dd, *J* = 8.0, 5.5 Hz, 0.25H), 4.08 (pd, *J* = 6.3, 1.7 Hz, 0.75H), 3.94 (sxt, *J* = 6.4 Hz, 0.25H), 3.74 (s, 0.75H), 3.67 (s, 2.25 H), 2.37-2.17 (m, 1.5H), 2.10-2.00 (m, 0.5H), 1.97 (ddt, *J* = 12.6, 6.3, 1.4 Hz, 0.75H), 1.94-1.86 (m, 0.25H), 1.69-1.58 (m, 1H), 1.30 (d, *J* = 6.4 Hz, 0.75H), 1.26 (d, *J* = 6.5 Hz, 2.25H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 172.43, 172.39, 150.19, 149.99, 146.46, 145.17, 128.86, 128.79, 124.34, 124.10, 61.92, 61.68, 58.04, 56.63, 52.73, 52.53, 33.03, 32.14, 29.55, 28.69, 21.75, 21.60

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_6S$ $[M+H]^+$: 329.0807, found 329.0800.

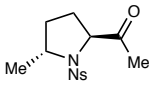


Synthesis of the reference compound: In a 25 mL recovery flask equipped with a magnetic stir bar were added methyl 5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxylate **12** (75.7 mg, 2.6:1 anti/syn, 0.23 mmol, 1.0 equiv.), cesium carbonate (300 mg, 0.92 mmol, 4.0 equiv.), MeCN (8.5 mL). The flask was backfilled with nitrogen 3x, and DMSO (171 μL) and thiophenol (83 μL, 0.81 mmol, 3.5 equiv.) were added. The reaction was stirred in 45 °C oil bath for 2 d. Upon completion, the reaction mixture as diluted with CH_2Cl_2, and washed with sat. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 3x. The combined organic layer was dried over K_2CO_3, filtered, and carefully condensed in vacuo at 0 °C. Purification by flash chromatography (50 mL silica, 200 mL 50% EtOAc/Hex→10% MeOH/CH_2Cl_2) followed by condensation in vacuo at 0 °C produced the free amine as a mixture with water and CH_2Cl_2. The water was removed using a separatory funnel and the aqueous layer extracted with CH_2Cl_2 1x. The combined organic layer was dried over K_2CO_3, filtered, and 4-fluorosulfonyl chloride (224 mg, 1.15 mmol, 5.0 equiv.) and triethylamine (160 μL, 1.15 mmol, 5.0 equiv.) were added directed, and the reaction was stirred overnight. Upon completion, the reaction mixture was washed with sat. $NaHCO_3$ and

the aqueous layer was extracted with CH_2Cl_2 2x. The combined organic layer was dried over $MgSO_4$, filtered, and condensed in vacuo. Purification by medium-pressure liquid chromatography (12 g silica, 100 column volumes 0% → 40% EtOAc/Hex) afforded methyl 1-((4-fluorophenyl)sulfonyl)-5-methylpyrrolidine-2-carboxylate as a mixture of diastereomers (30.4 mg, 0.101 mmol, 44% yield, 2:1 anti/syn). The ^{1}H NMR data of the syn product matched those reported in the literature[16].

^{1}H NMR: (400 MHz, $CDCl_3$)

δ 7.96-7.86 (m, 2H), 7.23-7.12 (m, 2H), 4.49-4.43 (m, 0.67H), 4.30 (dd, *J* = 8.1, 5.5 Hz, 0.33H), 4.10-4.01 (m, 0.67H), 3.85 (sxt, *J* = 6.4 Hz, 0.33H), 3.74 (s, 1H), 3.66 (s, 2H), 2.36-2.18 (m, 1.34H), 2.08-1.90 (m, 1.33H), 1.90-1.78 (m, 0.33H), 1.69-1.52 (m, 1H), 1.31 (d, *J* = 6.4 Hz, 1H), 1.22 (d, *J* = 6.5 Hz, 2H)



1-((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)ethan-1-one [13] According to the general oxidation procedure, (*S*)-1-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)ethan-1-one **S12** (59.7 mg, 0.20 mmol, 1.0 equiv.) in MeCN (0.4 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (1.4 mg, 0.0010 mmol, 0.005 equiv.), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (56.8 µL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M). Following oxidation, the crude was dissolved in CH_2Cl_2 (1.0 mL, 0.2 M), backfilled with nitrogen 3x, and placed into a -78 °C dry ice/acetone bath. DAST (26.4 µL, 32.2 mg, 0.20 mmol, 1.0 equiv.) was added, and the reaction was allowed to warm to room temperature while stirring for 1 h. The reaction was then placed back into -78 °C cold bath, where trimethylaluminum (2.0 M in hexanes, 300 µL, 0.60 mmol, 3.0 equiv.) was then added dropwise. The reaction mixture was stirred at -78 °C for 3 h, and then directly quenched with 1 M NaOH. Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→400 mL 20%→200 mL 30% EtOAc/Hex) to afford the product as a white solid. The stereochemistry was determined based on ^{1}H NMR, COSY, NOESY 1D, and NOESY 2D NMR methods.

Run 1 (44.3 mg, 0.142 mmol, 71% yield; 3:1 dr; 3% rsm by ^{1}H NMR)

Run 2 (46.0 mg, 0.147 mmol, 74% yield, 3:1 dr; 3% rsm by ^{1}H NMR)

Run 3 (45.8 mg, 0.147 mmol, 73% yield, 3:1 dr)

Average overall yield: 73% (2% rsm) ± 1.5, 3:1 dr

Characterization of major diastereomer **13**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 4.64 (dd, *J* = 9.4, 1.7 Hz, 1H), 4.02 (p, *J* = 6.6 Hz, 1H), 2.37-2.25 (m, 1H), 2.22 (s, 3H), 2.06 (tt, *J* = 12.5, 7.2 Hz, 1H), 1.85 (ddt, *J* = 13.2, 7.0, 1.8 Hz, 1H), 1.63-1.56 (m, 1H), 1.25 (d, *J* = 6.3 Hz, 3H)

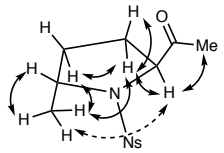
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 206.07, 150.02, 146.39, 128.94, 124.09, 67.95, 56.56, 31.96, 27.04, 26.81, 21.26

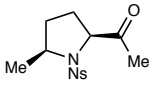
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_5S$ $[M+H]^+$: 313.0858, found 313.0862.

$[\alpha]_D^{24}$ = -35.5º (c = 0.81, CH_2Cl_2)



For COSY and NOESY see Supporting Information: Spectral Data



Characterization of minor diastereomer **S27**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.39 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 4.09 (t, *J* = 7.4 Hz, 1H), 3.85 (td, *J* = 6.8, 4.6 Hz, 1H), 2.37 (s, 3H), 2.05-1.95 (m, 1H), 1.86 (dq, *J* = 13.0, 6.9 Hz, 1H), 1.77-1.67 (m, 1H), 1.61-1.52 (m, 1H), 1.37 (d, *J* = 6.4 Hz, 3H)

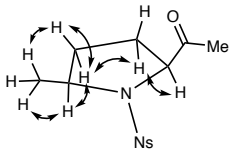
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 207.09, 150.46, 143.49, 129.06, 124.53, 69.30, 58.34, 32.66, 27.98, 25.94, 22.53

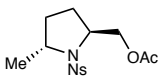
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_5S$ $[M+H]^+$: 313.0858, found 313.0869.

$[\alpha]_D^{24}$ = -69.6º (c = 0.57, CH_2Cl_2)



For COSY and NOESY see Supporting Information: Spectral Data



((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methyl acetate [14] According to the general oxidation and DAST-promoted methylation procedures, (*S*)-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methyl acetate **S13** (98.5 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (34.6 µL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with DAST (39.6 µL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→400 mL 20% EtOAc/Hex) to afford the product as a light yellow solid as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**, and by reducing **12** with $LiAlH_4$ and acetylating the resulting alcohol to form **14** (3:1 dr anti/syn) as a reference. The ^{1}H NMR data of the reduction/acetylation product matched those obtained via oxidative methylation.

Run 1 (69.2 mg, 0.202 mmol, 67% yield; 1.7:1 dr; 4.0 mg, 0.012 mmol, 4% rsm)

Run 2 (70.7 mg, 0.207 mmol, 69% yield, 1.7:1 dr; 10.4 mg, 0.0316 mmol, 11% rsm)

Run 3 (68.4 mg, 0.200 mmol, 67% yield, 1.7:1 dr; 13.1 mg, 0.0400 mmol, 13% rsm)

Average overall yield: 68% (9% rsm) ± 1.2, 1.7:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

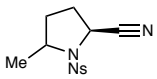
δ 8.36 (d, *J* = 8.4 Hz, 0.76H), 8.33 (d, *J* = 8.7 Hz, 1.24H), 8.09-8.00 (m, 2H), 4.37-4.28 (m, 0.62H), 4.20 (dd, *J* = 11.1, 4.8 Hz, 0.38H), 4.16-4.09 (m, 1H), 4.10-3.98 (m, 1.24H), 3.90 (td, *J* = 7.1, 3.6 Hz, 0.38H), 3.70 (sxt, *J* = 6.3 Hz, 0.38H), 2.21-2.01 (m, 1.52H), 2.07 (s, 1.14H), 1.96 (s, 1.86H), 1.86 (dd, *J* = 12.2, 6.1 Hz, 0.62H), 1.78-1.68 (m, 0.62H), 1.57 (dq, *J* = 9.8, 5.1 Hz, 1.24H), 1.36 (d, *J* = 6.3 Hz, 1.14H), 1.20 (d, *J* = 6.4 Hz, 1.86H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.77, 170.49, 150.29, 149.22, 147.69, 143.76, 128.84, 128.28, 124.49, 124.40, 66.26, 64.83, 59.85, 58.43, 58.30, 57.71, 32.32, 31.45, 27.46, 27.04, 23.00, 21.11, 20.99, 20.87

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{14}H_{19}N_2O_6S$ $[M+H]^+$: 343.0964, found 343.0960.



(2*S*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonitrile [15] To a 40 mL vial equipped with a stir bar were added (*S*)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonitrile **S14** (84.4 mg, 0.30 mmol, 1.0 equiv.), MeCN (0.6 mL, 0.5 M), and AcOH (257 µL, 4.50 mmol, 15.0 equiv.). The vial was then placed into ice bath while stirring. A 1 mL syringe was charged with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg,

0.0015 mmol, 0.005 equiv.) in MeCN (0.375 mL, 0.004 M to catalyst). Likewise, a 10 mL syringe was charged with H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Both syringes were fitted with 25G needles and solutions were added simutaneously using the same syringe pump over 1 h at 0 °C. The reaction mixture was then worked up according to the general oxidation procedure. Following work up, the crude was methylated with DAST (39.6 μL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 10%→600 mL 20% EtOAc/Hex) to afford the product as a white gel as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**.

Run 1 (42.8 mg, 0.145 mmol, 48% yield; 1.5:1 dr; 26% rsm by ^{1}H NMR)

Run 2 (38.2 mg, 0.129 mmol, 43% yield, 1.5:1 dr; 28% rsm by ^{1}H NMR)

Run 3 (38.3 mg, 0.130 mmol, 43% yield, 1.5:1 dr; 32% rsm by ^{1}H NMR)

Average overall yield: 45% (29% rsm) ± 2.9, 1.5:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

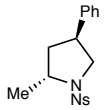
δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.6 Hz, 1.2H), 8.11 (d, *J* = 8.6 Hz, 0.8H), 4.76 (d, *J* = 7.5 Hz, 0.6H), 4.73 (dd, *J* = 8.2, 3.8 Hz, 0.4H), 4.04 (sxt, *J* = 6.5 Hz, 0.4H), 3.86 (p, *J* = 6.7 Hz, 0.6H), 2.44-2.31 (m, 0.6H), 2.30-2.09 (m, 2.4H), 1.91-1.77 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 1.8H), 1.31 (d, *J* = 6.3 Hz, 1.2H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.56, 150.47, 145.13, 143.62, 129.31, 128.64, 124.73, 124.44, 118.45, 116.93, 58.21, 56.20, 50.12, 49.62, 33.43, 32.72, 30.88, 29.41, 22.44, 21.60

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{11}H_{13}N_2O_4S$ $[M\text{-}CN]^+$: 269.0596, found 269.0589.



trans-2-methyl-1-((4-nitrophenyl)sulfonyl)-4-phenylpyrrolidine [(±)-16] According to a modified general oxidation procedure and the BF_3-promoted methylation procedure, 1-((4-nitrophenyl)sulfonyl)-3-phenylpyrrolidine **S15** (99.7 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 μL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (34.6 μL, 0.60 mmol, 2.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M) at 0 °C in ice bath. Following oxidation, the crude was methylated with trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) and BF_3•OEt_2 (74.0 μL, 0.60 mmol, 2.0 equiv.). Following workup, the crude material

was purified by medium-pressure liquid chromatography (24 g silica, 70 column volumes 0%→20% EtOAc/Hex) to afford the product as a light yellow solid as a mixture of diastereomers. The stereochemistry was determined by ^{1}H NMR, NOESY 2D, and COSY methods.

Run 1 (36.5 mg, 0.105 mmol, 35% yield, 6:1 dr; 31.6 mg, 0.0951 mmol, 32% rsm)

Run 2 (38.5 mg, 0.123 mmol, 37% yield, 6:1 dr; 26.4 mg, 0.0794 mmol, 26% rsm)

Run 3 (35.3 mg, 0.102 mmol, 34% yield, 7:1 dr; 21.1 mg, 0.0635 mmol, 21% rsm)

Average overall yield: 35% (26% rsm) ± 1.5, 6:1 dr

Characterization of major diastereomer **16**:

^{1}H NMR: (500 MHz, $CDCl_3$)

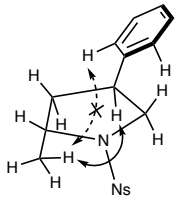
δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.28-7.18 (m, 3H), 7.06-7.03 (m, 2H), 3.99 (qd, *J* = 6.4, 4.3 Hz, 1H), 3.91 (dd, *J* = 9.4, 7.2 Hz, 1H), 3.56 (p, *J* = 8.8 Hz, 1H), 3.06 (t, *J* = 9.7 Hz, 1H), 1.97-1.90 (m, 2H), 1.44 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

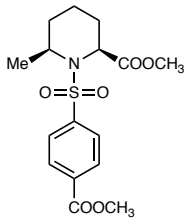
δ 150.19, 143.60, 139.42, 128.87, 128.65, 127.36, 126.96, 124.44, 56.64, 55.48, 41.67, 39.81, 23.44

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{19}N_2O_4S$ $[M+H]^+$: 347.1066, found 347.1059.



For COSY and NOESY see Supporting Information: Spectral Data



methyl (2*S*,6*S*)-1-((4-(methoxycarbonyl)phenyl)sulfonyl)-6-methylpiperidine-2-carboxylate [17]

Following the general oxidation and BF_3-promoted methylation, (*S*)-1-((4-(methoxycarbonyl)phenyl)sulfonyl)piperidine-2-carboxylate **S16** (103.1 mg, 0.302 mmol, 1.00 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-$MnCF_3$PDP (4.1 mg, 0.003 mmol, 0.01 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (86 µL, 1.51 mmol, 5 equiv.) in MeCN (3.75 mL), at -36 °C via the single addition protocol. Following oxidation, the crude was methylated with BF_3•OEt_2 (75 µL,

.604 mmol, 2.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by Medium Pressure Liquid Chromatography (40 g silica, liquid sample, gradient elution of 40 CV from 0% to 15% EtOAc/Hex) to afford the desired product as a pale white solid in an average of 47% yield.

Run 1 (48.3 mg, 0.136 mmol, 45% yield; 0% rsm and >20:1 dr by ^{1}H NMR. 20% C=C observed by crude NMR)

Run 2 (51.5 mg, 0.145 mmol, 48% yield; 0% rsm and >20:1 dr by ^{1}H NMR. 23% C=C observed by crude NMR)

Run 3 (50.4 mg, 0.142 mmol, 47% yield; 0% rsm and >20:1 dr by ^{1}H NMR. 24% C=C observed by crude NMR)

Average overall yield: 47% (0% rsm) ± 1.2, >20:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 4.82 (d, *J* = 5.0 Hz, 1H), 4.12 (tq, *J* = 6.9, 3.8 Hz, 1H), 3.95 (s, 3H), 3.67 (s, 3H), 2.29 (d, *J* = 11.0 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.53 – 1.37 (m, 5H), 1.05 (d, *J* = 7.1 Hz, 3H)

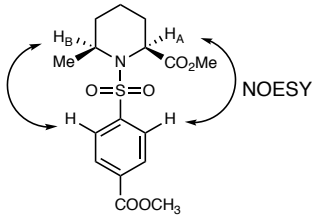
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 172.54, 165.84, 145.13, 133.68, 130.21, 127.38, 52.74, 52.68, 52.39, 49.07, 29.61, 25.90, 18.30, 15.14

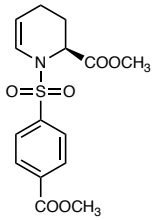
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{16}H_{21}NNaO_6S$ $[M+Na]^+$: 378.0987, found 358.0993.

$[\alpha]_D^{24}$ = -27.8 (c = 1.00, EtOH)



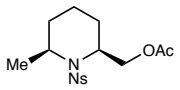
For NOESY and decoupling see Supporting Information: Spectral Data. Both H_A and H_B were shown to be equatorial and *cis* to each other because of their coupling constants and NOESY correlations.



The enamine was observed in an average of 22% yield (see above). When submitting the substrate to the same conditions but using DAST (1 equiv.) as the activator, 60% enamine was isolated with trace (2%) product.

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.09-5.03 (m, 1H), 4.76-4.73 (m, 1H), 3.97 (s, 3H), 3.66 (s, 3H), 2.23 (d, *J* = 13.7 Hz, 1H), 1.97-1.84 (m, 2H), 1.47 (dt, *J* = 17.0, 7.9 Hz, 1H).



((2*S*,6*S*)-6-methyl-1-((4-nitrophenyl)sulfonyl)piperidin-2-yl)methyl acetate [18] Following the general oxidation and DAST-promoted methylation**,** (*S*)-(1-((4-nitrophenyl)sulfonyl)piperidin-2-yl)methyl acetate **S17** (103.4 mg, 0.302 mmol, 1.00 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (86 µL, 1.51 mmol, 5 equiv.) in MeCN (3.75 mL), at -36 °C via the single addition protocol. Following oxidation, the crude was subjected to DAST (40 µL, 0.303 mmol, 1.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 36 CV 0% to 12%, 10 CV from 12% to 15% EtOAc/Hex) to afford the desired product as a white powder in an average of 64% yield.

Run 1: 65.6 mg, 0.184 mmol, 61% yield; 0% rsm and 14% C=C by ^{1}H NMR and >20:1 dr by ^{1}H NMR.

Run 2: 70.0 mg, 0.196 mmol, 65% yield; 0% rsm and 9% C=C by ^{1}H NMR and >20:1 dr by ^{1}H NMR.

Run 3: 69.6 mg, 0.195 mmol, 65% yield; 0% rsm and 12% C=C by ^{1}H NMR and >20:1 dr by ^{1}H NMR.

Average overall yield: 64% yield (0% rsm) ± 1.9.

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 4.35 (dd, *J* = 10.6, 8.3 Hz, 1H), 4.27 (q, *J* = 6.9 Hz, 1H), 4.12 (p, *J* = 5.6 Hz, 1H), 4.07 (dd, *J* = 10.6, 6.6 Hz, 1H), 2.09 (s, 3H), 1.73 – 1.57 (m, 2H), 1.52 – 1.43 (m, 1H), 1.39 (dt, *J* = 14.2, 3.8 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.30 – 1.22 (m, 2H).

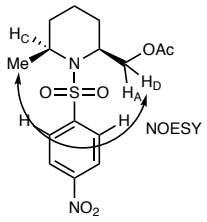
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 171.02, 150.13, 147.52, 128.15, 124.73, 64.78, 51.04, 48.77, 29.57, 25.08, 22.20, 21.24, 13.79.

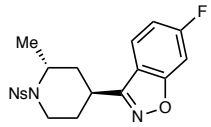
HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{15}H_{20}N_2NaO_6S$ $[M+Na]^+$: 379.0940, found 379.0932

$[\alpha]_D^{24}$ = -7.29 (c = 1.00, EtOH)



For NOESY see Supporting Information: Spectral Data



6-fluoro-3-(trans-2-methyl-1-((4-nitrophenyl)sulfonyl)piperidin-4-yl)benzo[*d*]isoxazole [(±)-19]

According to modified general oxidation and DAST-promoted methylation procedures, in a 40-mL vial were added 6-fluoro-3-(1-((4-nitrophenyl)sulfonyl)piperidin-4-yl)benzo[*d*]isoxazole **S18** (121.6 mg, 0.30 mmol, 1.0 equiv.), 1:1.7 MeCN/CH_2Cl_2 (2.7 mL, 0.11 M), and AcOH (257 μL, 4.50 mmol, 15.0 equiv.). H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in 4:1 MeCN/CH_2Cl_2 (3.75 mL) and (*S*,*S*)-Mn(CF_3PDP) (40.7 mg, 0.03 mmol, 0.10 equiv.) in 4:1 MeCN/CH_2Cl_2 (0.37 mL) were transferred to 10 mL and 1 mL synringes and added concurrently via a syringe pump into the vial in 1 h at room temperature. Following oxidation and workup, the oxidation products were isolated from the starting material through flash chromatography (50 mL silica, 200 mL 2% MeOH/CH_2Cl_2), and methylated with DAST (39.6 μL, 48.3 mg, 0.30 mmol, 1.0 equiv.) (florination at -78 °C for 10 min, then room temperature for 50 min) and trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, 300 mL 20% EtOAc/Hex) to afford the product as a white solid. The starting material was resubjected to the reaction conditions 1x. The stereochemistry was determined based on ^{1}H NMR, COSY, and NOESY 2D NMR methods.

Run 1 (1st cycle: 37.7 mg, 0.0898 mmol, 30% yield, >20:1 dr; 42.2 mg, 0.104 mmol, 35% rsm. 2nd cycle: 10.0 mg, 0.0238 mmol, 23% yield, >20:1 dr; 17.7 mg, 0.0438 mmol, 42% rsm. Overall: 47.7 mg, 0.114 mmol, 38% yield, >20:1 dr; 17.7 mg, 0.0438 mmol, 15% rsm)

Run 2 (1st cycle: 34.8 mg, 0.0830 mmol, 28% yield, >20:1 dr; 33.0 mg, 0.0814 mmol, 27% rsm. 2nd cycle: 11.9 mg, 0.0283 mmol, 35% yield, >20:1 dr; 11.4 mg, 0.0281 mmol, 35% rsm. Overall: 46.7 mg, 0.111 mmol, 37% yield, >20:1 dr; 11.4 mg, 0.0281 mmol, 9% rsm)

Run 3 (1st cycle: 37.7 mg, 0.0898 mmol, 30% yield, >20:1 dr; 35.6 mg, 0.0878 mmol. 29% rsm. 2nd cycle: 6.3 mg, 0.015 mmol, 17% yield, >20:1 dr; 17.2 mg, 0.0424 mmol, 48% rsm. Overall: 44.0 mg, 0.105 mmol, 35% yield, >20:1 dr; 17.2 mg, 0.0424 mmol, 14% rsm)

Average overall yield: 37% (13% rsm) ± 1.5, >20:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.52 (dd, *J* = 8.7, 5.0 Hz, 1H), 7.26-7.22 (m, 1H), 7.06 (td, *J* = 8.8, 2.1 Hz, 1H), 4.53 (p, *J* = 6.3 Hz, 1H), 4.05-3.96 (m, 1H), 3.45 (tt, *J* = 12.4, 3.5 Hz, 1H), 3.27 (td, *J* = 13.4, 2.7 Hz, 1H), 2.16-2.05 (m, 2H), 1.99-1.91 (m, 1H), 1.88 (qd, *J* = 13.0, 4.6 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

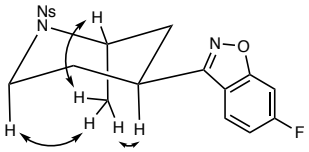
δ 164.27 (d, *J* = 251.3 Hz), 164.19 (d, *J* = 14.0 Hz), 160.06, 150.11, 147.01, 128.28, 124.69, 122.13 (d, *J* = 11.1 Hz), 116.85, 112.90 (d, *J* = 25.3 Hz), 97.88 (d, *J* = 26.9 Hz), 48.81, 40.13, 35.32, 30.25, 28.85

^{19}F NMR: (470 MHz, $CDCl_3$)

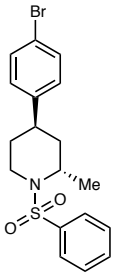
δ -108.67 (td, *J* = 8.6, 5.1 Hz)

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{19}N_3O_5SF$ $[M+H]^+$: 420.1029, found 420.1041.



For COSY and NOESY see Supporting Information: Spectral Data



trans-4-(4-bromophenyl)-2-methyl-1-(phenylsulfonyl)piperidine [(±)-20] Following the general oxidation and BF_3-promoted methylation procedures, 4-(4-bromophenyl)-1-(phenylsulfonyl)piperidine **S19** (114.9 mg, 0.302 mmol, 1.00 equiv.) in 4:1 MeCN/DCM (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (8.2 mg, 0.006 mmol, 0.02 equiv.), acetic acid (259 µL, 4.53 mmol, 15.0 equiv.), and H_2O_2 (86 µL, 1.5 mmol, 5 equiv., 50 wt.% in H_2O) in 4:1 MeCN/DCM (3.75 mL), at 0 °C via the single addition protocol. Following oxidation, the crude was methylated with BF_3•OEt_2 (75 µL, 0.60 mmol, 2.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 20 CV 0% to 5%, 15 CV 5%, 10 CV 5% to 10% EtOAc/Hex) to produce the desired compound as a white powder.

Run 1: 42.9 mg, 0.109 mmol, 36% yield; 39% rsm and > 20:1 dr by ^{1}H NMR

Run 2: 44.2 mg, 0.112 mmol, 37% yield; 40% rsm and > 20:1 dr by ^{1}H NMR

Run 3: 45.2 mg, 0.114 mmol, 38% yield; 33% rsm and > 20:1 dr by ^{1}H NMR

Average overall yield: 39% yield (37% rsm) ± 0.8, > 20:1 dr

^{1}H NMR: (500 MHz, Chloroform-*d*)

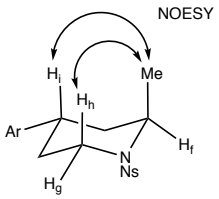
δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.43 (p, *J* = 7.1, 1H), 3.91 (ddd, *J* = 13.8, 4.8, 2.2 Hz, 1H), 3.13 (td, *J* = 13.2, 2.7 Hz, 1H), 2.81 (tt, *J* = 12.7, 3.7 Hz, 1H), 1.78 – 1.66 (m, 2H), 1.63-1.60 (m, 1H), 1.51 (qd, *J* = 12.9, 4.7 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 3H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

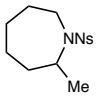
δ 144.17, 141.34, 132.49, 131.75, 129.24, 128.60, 127.12, 120.31, 48.78, 40.29, 37.94, 35.69, 32.68, 15.91

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{18}H_{21}BrNO_2S$ $[M+H]^+$: 394.0476, found 394.0470.



For COSY and NOESY see Supporting Information: Spectral Data



2-methyl-1-((4-nitrophenyl)sulfonyl)azepane [21] Following the general oxidation and BF_3-promoted methylation procedures, 1-((4-nitrophenyl)sulfonyl)azepane **S20** (85.9 mg, 0.302 mmol, 1 equiv.) in MeCN/DCM (1.7:1 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (4.1 mg, 0.003 mmol, 0.01 equiv.), acetic acid (259 µL, 4.53 mmol, 15.0 equiv.), and H_2O_2 (86 µL, 1.5 mmol, 5 equiv., 50 wt.% in H_2O) in MeCN/DCM (2.6:0.9 mL), at -36 °C via the single addition protocol.. Following oxidation, the crude was methylated with BF_3•OEt_2 (75 µL, .60 mmol, 2.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 0% → 1% → 2% → 3% → 400 mL 4% ethyl acetate in hexanes) to afford the desired product as a pale white solid.

Run 1: 36.9 mg, 0.124 mmol, 41% yield; 10% rsm by ^{1}H NMR

Run 2: 34.2 mg, 0.115 mmol, 38% yield; 5% rsm by ^{1}H NMR

Run 3: 36.8 mg, 0.123 mmol, 41% yield; 5% rsm by ^{1}H NMR

Average overall yield: 40% yield (7% rsm) ± 1.4

The hemiaminal during C–H oxidation was likely opened and subsequently underwent overoxidation to the carboxylic acid, resulting in lower mass balance[1].

^{1}H NMR: (500 MHz, Chloroform-*d*)

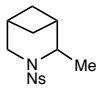
δ 8.34 (d, 2H, *J* = 7.2 Hz), 8.03 (d, 2H, *J* = 7.0 Hz), 4.09-4.00 (m, 1H), 3.76 (dt, 1H, *J* = 15.2, 3.7 Hz), 2.96 (ddd, 1H, *J* = 15.2, 11.7, 2.1 Hz), 2.06 (m, 1H), 1.76 (m, 1H), 1.72-1.58 (m, 2H), 1.22 (m, 4H), 0.98 (d, 3H, *J* = 5.2 Hz)

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 149.80, 148.05, 128.32, 124.41, 53.67, 43.00, 37.19, 29.80, 29.54, 24.54, 20.16

HRMS: (EI HR MS EI+)

m/z calculated for $C_{13}H_{18}N_2O_4S$ [M]: 298.0987, found 298.0988.



2-methyl-3-((4-nitrophenyl)sulfonyl)-3-azabicyclo[3.1.1]heptane [22] Following the general oxidation and BF_3-promoted methylation procedures, 3-((4-nitrophenyl)sulfonyl)-3-azabicyclo[3.1.1]heptane **S21** (85.3 mg, 0.302 mmol, 1 equiv.) in MeCN/DCM (1:0.25 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), acetic acid (259 µL, 4.53 mmol, 15.0 equiv.), and H_2O_2 (34 µL, 0.60 mmol, 2 equiv., 50 wt.% in H_2O) in MeCN/DCM (2.8:0.7 mL), at 0 °C via the single addition protocol. Following oxidation, the crude was methylated with BF_3•OEt_2 (75 µL, .60 mmol, 2.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (70 mL silica, loaded with DCM, gradient elution 200 mL 0% → 1% → 2% → 3% → 4% → 5% → 6% ethyl acetate in hexanes) to afford the desired product as a pale white solid.

Run 1: 35.0 mg, 0.118 mmol, 39% yield; 6% rsm by ^{1}H NMR; 2% dimethylated was isolated.

Run 2: 36.7 mg, 0.124 mmol, 41% yield; 10% rsm by ^{1}H NMR; 1% dimethylated was isolated.

Run 3: 34.7 mg, 0.117 mmol, 39% yield; 6% rsm by ^{1}H NMR; 3% dimethylated was isolated.

Average overall yield: 40% yield (7% rsm) ± 0.9

The hemiaminal during C—H oxidation was likely opened and subsequently underwent overoxidation to the carboxylic acid, resulting in lower mass balance[1].

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 4.02 (qd, *J* = 6.3, 3.6 Hz, 1H), 3.57 (t, *J* = 11.0 Hz, 1H), 3.53 (dd, *J* = 26.6, 10.9 Hz, 1H), 2.36 (qdd, *J* = 5.8, 3.6, 1.6 Hz, 1H), 2.21 (qd, *J* =

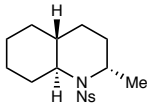
6.0, 3.6 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.92 (dt, *J* = 9.6, 5.9 Hz, 1H), 1.50 (dd, *J* = 10.0, 8.1 Hz, 1H), 1.40 (d, *J* = 6.3 Hz, 3H), 0.62 (dd, *J* = 9.7, 8.1 Hz, 1H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 150.07, 145.04, 128.65, 124.49, 57.44, 51.30, 38.77, 32.96, 30.42, 28.55, 20.78

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{13}H_{17}N_2O_4S$ $[M+H]^+$: 297.0909, found 297.0912.



***rel*-(2*S*,4a*R*,8a*S*)-2-methyl-1-((4-nitrophenyl)sulfonyl)decahydroquinoline [(±)-23]** Following the general oxidation and BF_3-promoted procedures, 1-((4-nitrophenyl)sulfonyl)-trans-decahydroquinoline **S22** (97.9 mg, 0.302 mmol, 1.00 equiv.) in MeCN/DCM (1.3 mL/0.3 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), acetic acid (259 µL, 4.53 mmol, 15.0 equiv.), and H_2O_2 (34 µL, 0.604 mmol, 2 equiv., 50 wt.% in H_2O) in MeCN/DCM (2.8 mL/0.7 mL), at -36 °C via the single addition protocol. Following oxidation, the crude was methylated with BF_3•OEt_2 (75 µL, .60 mmol, 2.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, DCM loaded, gradient elution 200 mL 0% → 1% → 2% → 3% → 4% → 400 mL 5% → 200 mL 20% EtOAc/Hex) to afford the desired product as a white solid.

Run 1: 40.9 mg, 0.121 mmol, 40% yield; 12 % rsm and 5:1 dr by ^{1}H NMR.

Run 2: 41.0 mg, 0.121 mmol, 40% yield; 10% rsm and 5:1 dr by ^{1}H NMR.

Run 3: 38.6 mg, 0.114 mmol, 38% yield; 20% rsm and 5:1 dr by ^{1}H NMR.

Average overall yield: 39% yield (14% rsm) ± 0.9, 5:1 dr

The product has poor solubility, which resulted in lower yields during isolation. A higher yield was obtained when the product was isolated as a mixture with the starting material. Following workup, the crude material was purified by flash chromatography (50 mL silica, DCM loaded, gradient elution 200 mL 10% → 20% EtOAc/Hex) to give a mixture of the desired product and the starting material.

Run 1: 46.0 mg, 0.136 mmol, 45% yield; 14 % rsm; 5:1 dr by ^{1}H NMR.

Run 2: 45.8 mg, 0.135 mmol, 45% yield; 13% rsm; 5:1 dr by ^{1}H NMR.

Run 3: 48.0 mg, 0.142 mmol, 47% yield; 19% rsm; 5:1 dr by ^{1}H NMR.

Average overall yield: **46% yield (15% rsm) ± 0.9, 5:1 dr**

^{1}H NMR: (500 MHz, Chloroform-*d*)

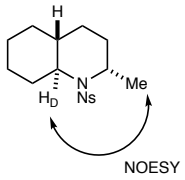
δ 8.31 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 4.71 (qdd, *J* = 7.0, 5.1, 2.2 Hz, 1H), 3.09 (ddd, *J* = 11.7, 10.0, 3.5 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.90 (tt, *J* = 13.4, 4.8 Hz, 1H), 1.75 – 1.55 (m, 5H), 1.48 – 1.38 (m, 2H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.34 – 1.21 (m, 1H), 1.22 – 1.08 (m, 2H), 1.02 (dddd, *J* = 13.0, 11.1, 7.9, 3.6 Hz, 1H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

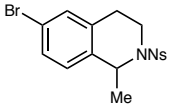
δ 150.57, 149.67, 128.09, 124.29, 59.33, 51.66, 41.61, 33.43, 30.92, 30.88, 27.00, 26.43, 25.38, 17.17

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{16}H_{23}N_2O_4S$ $[M+H]^+$: 339.1379, found 339.1387.



For NOESY see Supporting Information: Spectral Data



6-bromo-1-methyl-2-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline [24] Following the general oxidation and BF_3-promoted methylation protocols, 6-bromo-2-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline **S23** (120 mg, 0.302 mmol, 1 equiv.) in MeCN/DCM (1.7 mL:1 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (4.1 mg, 0.0030 mmol, 0.01 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (86 µL, 1.5 mmol, 5 equiv.) in MeCN/DCM (2.6 mL:0.9 mL), at 0 °C via the single addition protocol. Following oxidation, the crude mixture was methylated with BF_3•OEt_2 (75 µL, 0.604 mmol, 2 equiv.) and $AlMe_3$ (450 µL, 0.90 mmol, 3 equiv.). Following workup, the resulting oil was purified using liquid chromatography (50 mL silica, loaded with DCM, 200 mL 0% → 2% → 4% → 600 mL 5% EtOAc/Hex) to afford the desired product as a transparent oil.

Run 1: 54.5 mg, 0.133 mmol, 44% yield; 5% rsm by ^{1}H NMR

Run 2: 56.0 mg, 0.136 mmol, 45% yield; 10% rsm by ^{1}H NMR

Run 3: 56.9 mg, 0.138 mmol, 46% yield; 5% rsm by ^{1}H NMR

Average overall yield: 45% yield (7% rsm) ± 0.8

The product has poor solubility which resulted in lower yields during isolation. A higher yield was obtained when the product was isolated as a mixture with the starting material. Following workup, the

crude material was purified by flash chromatography (50 mL silica, DCM loaded, gradient elution 100 mL 0% → 300 mL 15% EtOAc/Hex) to give a mixture of the desired product and the starting material.

Run 1: 62.1 mg, 0.151 mmol, 50% yield; 7 % rsm by ^{1}H NMR

Run 2: 62.3 mg, 0.151 mmol, 50% yield; 6 % rsm by ^{1}H NMR

Run 3: 65.8 mg, 0.160 mmol, 53% yield; 6 % rsm by ^{1}H NMR

Average overall yield: **51% yield (6% rsm) ± 1.4.**

^{1}H NMR: (500 MHz, Chloroform-*d*)

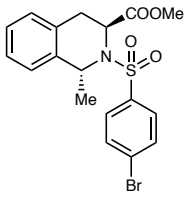
δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.30 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.12 (q, *J* = 6.8 Hz, 1H), 4.01 – 3.88 (m, 1H), 3.45 (ddd, *J* = 13.8, 10.5, 5.3 Hz, 1H), 2.76 – 2.61 (m, 2H), 1.47 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 150.04, 146.88, 136.14, 134.56, 132.06, 129.98, 128.41, 128.11, 124.52, 120.82, 52.26, 38.55, 27.75, 23.54

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{16}H_{16}BrN_2O_4S$ $[M+H]^+$: 411.0014, found 411.0016.



methyl (1*R*,3*S*)-2-((4-bromophenyl)sulfonyl)-1-methyl-1,2,3,4-tetrahydroisoquinoline-3-carboxylate [25] Following the general oxidation and BF_3-promoted methylation protocols, methyl (*S*)-2-((4-bromophenyl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate **S24** (123.9 mg, 0.302 mmol, 1 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (8.1 mg, 0.0060 mmol, 0.02 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (86 µL, 1.5 mmol, 5 equiv.) in MeCN (3.75 mL), at -36 °C via the single addition protocol. Following oxidation, the crude mixture was methylated with BF_3•OEt_2 (75 µL, 0.604 mmol, 2 equiv.) and $AlMe_3$ (450 µL, 0.90 mmol, 3 equiv.). Following workup, the resulting oil was purified by MPLC (40 g silica, wet loaded with DCM, gradient elution 40 CV 0% to 20% EtOAc/Hex) to afford the desired product as a white solid.

Run 1: 64.7 mg, 0.152 mmol, 50% yield; 10% rsm and 2:1 dr by ^{1}H NMR.

Run 2: 56.0 mg, 0.151 mmol, 50% yield; 10% rsm and 2:1 dr by ^{1}H NMR.

Run 3: 61.5 mg, 0.145 mmol, 48% yield; 11% rsm and 2:1 dr by ^{1}H NMR.

Average overall yield: 50% yield (10% rsm) ± 0.5, 2:1 dr

Characterization of major diastereomer:

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 6.0 Hz, 1H), 7.16 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 – 7.03 (m, 2H), 5.05 (q, *J* = 6.8 Hz, 1H), 4.89 (dd, *J* = 5.4, 3.9 Hz, 1H), 3.44 (s, 3H), 3.33 (dd, *J* = 15.6, 5.4 Hz, 1H), 3.19 (dd, *J* = 15.6, 3.9 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H)

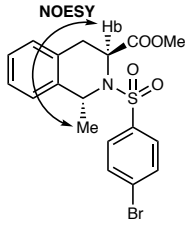
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 171.41, 140.15, 139.28, 132.31, 130.41, 129.22, 128.48, 127.80, 127.74, 127.38, 126.15, 56.49, 54.71, 52.43, 32.73, 26.13

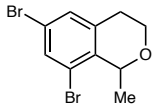
HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{18}H_{19}BrNO_4S$ $[M-H]^+$: 424.0218, found. 424.0204.

$[\alpha]_D^{24}$ = -5.888 (c = 1.00, EtOH)



For NOESY see Supporting Information: Spectral Data



6,8-dibromo-1-methylisochromane [26] Following the general oxidation and DAST-promoted methylation**,** 6,8-dibromoisochromane **S25** (88.2 mg, 0.302 mmol, 1.00 equiv.) in MeCN/DCM (1.7 mL / 1 mL respectively) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), acetic acid (259 µL, 4.53 mmol, 15 equiv.), and H_2O_2 (34 µL, 0.604 mmol, 2 equiv.) in 4:1 MeCN/DCM (2.8 mL/0.7 mL), at 0 °C and via the single addition protocol. Following oxidation, the crude was subjected to DAST (40 µL, 0.303 mmol, 1.0 equiv.) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 0% → 5% → 10% ethyl acetate in hexanes) to afford the desired product as a pale yellow oil.

Run 1: 63.8 mg, 0.208 mmol, 69% yield; 5% rsm by ^{1}H NMR.

Run 2: 71.2 mg, 0.232 mmol, 77% yield; 5% rsm by ^{1}H NMR.

Run 3: 70.2 mg, 0.230 mmol, 76% yield; 5% rsm by ^{1}H NMR.

Average overall yield: 74% yield (5% rsm) ± 3.6.

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.54 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 4.98 (q, *J* = 6.5 Hz, 1H), 4.05 (ddd, *J* = 11.7, 9.4, 4.2 Hz, 1H), 3.83 (ddd, *J* = 11.6, 5.9, 3.6 Hz, 1H), 2.91 (m, 1H), 2.71 (dt, *J* = 16.5, 4.0 Hz, 1H), 1.55 (d, *J* = 6.5 Hz, 3H).

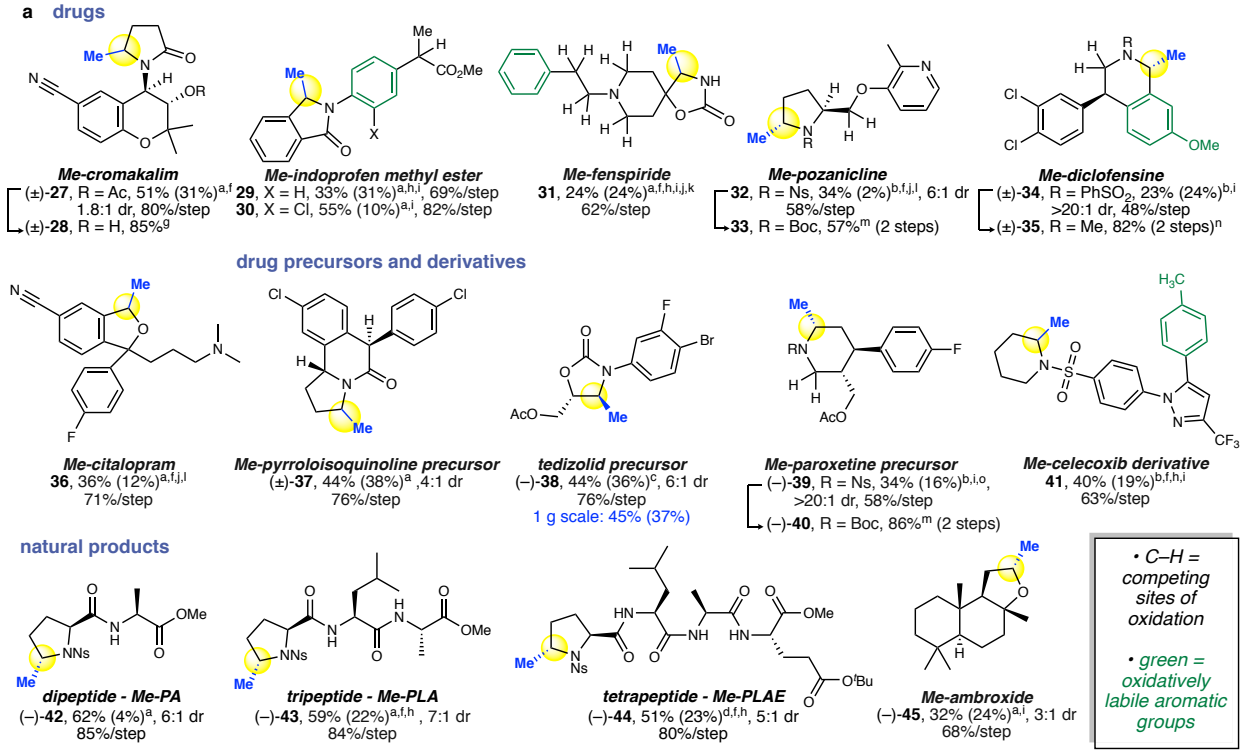
^{13}C NMR: (126 MHz, Chloroform-*d*)

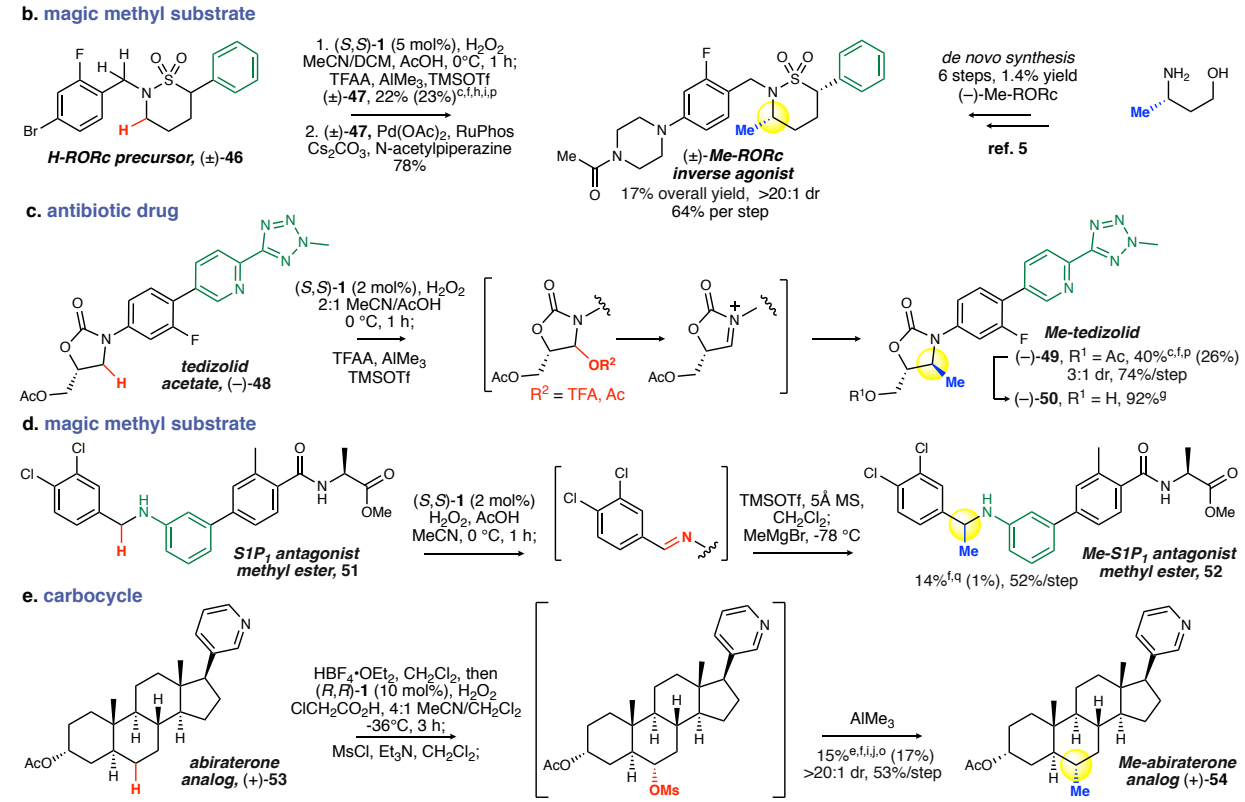
δ 137.95, 137.72, 133.31, 131.25, 121.86, 120.34, 71.18, 58.83, 28.66, 19.66

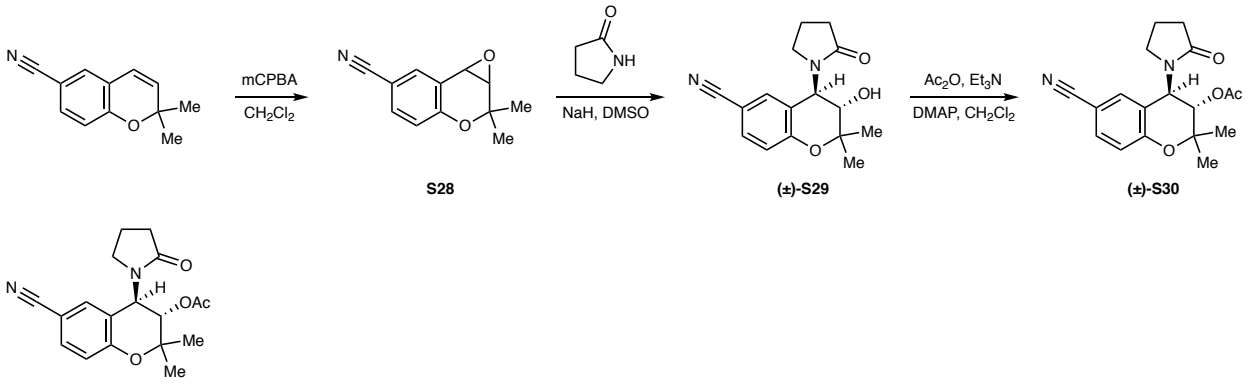
HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{10}H_9Br_2O$ [M-H]: 302.9020, found 302.9013.

V. Preparation and characterization of newly reported starting materials for Figure 4







trans-6-cyano-2,2-dimethyl-4-(2-oxopyrrolidin-1-yl)chroman-3-yl acetate [(±)-S30] In a 100-mL round-bottom flask were added 2,2-dimethyl-4a,8a-dihydro-2*H*-chromene-6-carbonitrile (878 mg, 4.74 mmol, 1.0 equiv) and CH_2Cl_2 (18 mL). The solution was placed into an ice bath, and mCPBA (70 wt%, 1.4 g, 5.69 mmol, 1.2 equiv.) was added in one portion. The reaction was stirred overnight and quenched with sat. $Na_2S_2O_3$ and then sat. $NaHCO_3$. Purification by flash column chromatography (50 mL silica, 200 mL 20%→30% EtOAc/Hex) afforded 2,2-dimethyl-1a,7b-dihydro-2*H*-oxireno[2,3-*c*]chromene-6-carbonitrile **S29** as a pale-white oil (954 mg, 4.74 mmol, quantitative yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 2.1 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 4.4 Hz, 1H), 3.54 (d, *J* = 4.3 Hz, 1H), 1.60 (s, 3H), 1.30 (s, 3H). In a 100-mL round-bottom flask carrying **S28** was added 2-pyrrolidinone (403 mg, 4.74 mmol, 1.0 equiv.) and DMSO (28 mL). NaH (60 wt%, 190 mg, 4.74 mmol, 1.0 equiv.) was then added upon stirring. The reaction was stirred for 6 h, quenched with water, and extracted with EtOAc 3x. The organic layer was washed with water 2x and brine 1x, and dried over $MgSO_4$. Purification by medium-pressure liquid chromatography (40 g silica, 50 column volumes 40%→100% EtOAc/Hex→10 column volumes EtOAc) afforded trans-3-hydroxy-2,2-dimethyl-4-(2-oxopyrrolidin-1-yl)chromane-6-carbonitrile **(±)-S29** as a white powder (755 mg, 2.64 mmol, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.44 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.23 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.11 (d, *J* = 6.8 Hz, 1H), 3.74 (dd, *J* = 10.4, 6.6 Hz, 1H), 3.37 (dt, *J* = 9.5, 7.6 Hz, 1H), 3.04 (td, *J* = 8.9, 4.4 Hz, 1H), 2.62 – 2.51 (m, 2H), 2.21 – 2.01 (m, 2H), 1.53 (s, 3H), 1.27 (s, 3H). In a 100-mL round-bottom flask carrying **S29** (385 mg, 1.34 mmol, 1.0 equiv.) was added DMAP (16.4 mg, 0.134 mmol, 0.1 equiv.), CH_2Cl_2 (10 mL), Et_3N (934 μL, 678 mg, 6.70 mmol, 5.0 equiv.), and Ac_2O (380 μL, 410 mg, 4.02 mmol, 3.0 equiv.). The reaction was stirred overnight, and then quenched with sat. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 2x and the organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flash chromatography (50 mL silica, 300 mL 40%→60% EtOAc/Hex) afforded the product as a white powder (326 mg, 0.99 mmol, 74% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

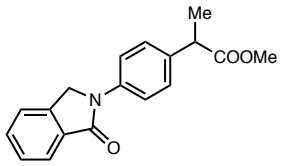
δ 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.26 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 10.1 Hz, 1H), 3.37 (dt, *J* = 9.3, 7.3 Hz, 1H), 2.93 (dt, *J* = 9.2, 6.7 Hz, 1H), 2.53 (dt, *J* = 17.1, 7.6 Hz, 1H), 2.41 (dt, *J* = 17.0, 8.4 Hz, 1H), 2.11 (s, 3H), 2.01 (p, *J* = 7.5 Hz, 2H), 1.43 (s, 3H), 1.35 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

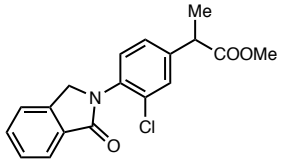
δ 176.97, 170.40, 157.15, 133.40, 132.02, 120.56, 119.14, 118.88, 105.02, 78.66, 69.80, 49.72, 42.60, 31.20, 26.39, 21.02, 19.63, 18.32

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{18}H_{21}N_2O_4$ $[M+H]^+$: 329.1501, found 329.1511.



methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoate [S31] Prepared according to literature and the NMR data matched those reported[17].



methyl 2-(3-chloro-4-(1-oxoisoindolin-2-yl)phenyl)propanoate [S32] In a 50-mL recovery flask was added methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoate **S31** (713 mg, 2.41 mmol, 1.0 equiv.), toluene (12 mL), trifluoroacetic acid (92 µL, 137 mg, 1.21 mmol, 0.5 equiv.), and *N*-chlorosuccinimide (484 mg, 3.62 mmol, 1.5 equiv.). The reaction was stirred at room temperature overnight, quenched with $NaHCO_3$, and extracted with CH_2Cl_2 3x. The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by medium-pressure liquid chromatography (40 g silica, 55 column volumes 0%→50% EtOAc/Hex) afforded the product as a white powder (544 mg, 1.65 mmol, 68% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.96 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.80 (s, 2H), 3.75 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

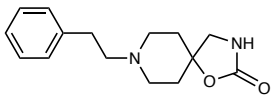
δ 174.26, 168.29, 142.12, 141.77, 134.90, 132.81, 132.16, 132.04, 130.19, 129.85, 128.41, 127.25, 124.62, 123.01, 52.46, 52.35, 45.04, 18.60

IR: (cm^{-1})

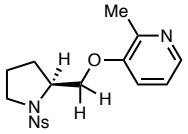
2955, 1733, 1683, 1500, 1469, 1447, 1433, 1399, 1336, 1302, 1255, 1212, 1197, 1168, 1100, 1078, 1046, 1016, 972, 921, 895, 867, 838, 800, 784, 758, 735, 682, 609, 578, 510, 484, 455

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{18}H_{17}NO_3Cl$ $[M+H]^+$: 330.0897, found 330.0897.



8-phenethyl-1-oxa-3,8-diazaspiro[4.5]decan-2-one [S33] Purchased from Sigma Aldrich as the hydrochloride salt.



(*S*)-2-methyl-3-((1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methoxy)pyridine [S34] According to the general procedure for nosyl protection, L-prolinol (425 mg, 4.20 mmol, 1 equiv.) was reacted with DMAP (51.3 mg, 0.420 mmol, 0.1 equiv.), Et_3N (644 µL, 467 mg, 4.62 mmol, 1.1 equiv.), and NsCl (1.02 g, 4.62 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elusion 200 mL 2%→5% MeOH/CH_2Cl_2) to afford (*S*)-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methanol with minor byproducts (roughly 970 mg, 3.39 mmol, 81% yield). In a separate 100-mL recovery flask triphenylphosphine (1.34 g, 5.09 mmol, 1.5 equiv.) and THF (13 mL) were added. The reaction was cooled to 0 °C, where DEAD (799 µL, 886 mg, 5.09 mmol, 1.5 equiv.) was added dropwise, and the reaction was stirred for 30 min. (*S*)-(1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methanol and 2-methylpyridin-3-ol (555 mg, 5.09 mmol, 1.5 equiv.) in THF (5 mL) were then both added to the reaction mixture, and the reaction was stirred overnight at room temperature. The solvent was removed in vacuo, and the brown crude was repeatedly washed with hexanes and then CH_2Cl_2. The CH_2Cl_2 wash was recrystallized by slowly evaporating CH_2Cl_2 in the fume hood, and the resulting crystals were washed with EtOAc 3x to afford the product as off-white crystals (434 mg, 1.15 mmol, 23% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.11 (dd, *J* = 4.5, 1.7 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.21-7.06 (m, *J* = 2H), 4.30 – 4.20 (m, 1H), 4.06 – 3.96 (m, 2H), 3.59 (ddd, *J* = 10.7, 7.1, 4.0 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.43 (s, 3H), 2.14 – 1.98 (m, 2H), 1.85 – 1.67 (m, 2H).

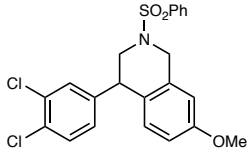
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 152.64, 150.33, 148.68, 143.27, 141.06, 128.70, 124.58, 121.96, 117.50, 69.69, 58.87, 49.65, 29.13, 24.28, 19.62

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{20}N_3O_5S$ $[M+H]^+$: 378.1124, found 378.1116.

$[\alpha]_D^{24}$ = -149.7º (c = 1.00, CH_2Cl_2)



4-(3,4-dichlorophenyl)-7-methoxy-2-(phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline [S35]

Diclofensine was synthesized according to literature precedent[18]. Diclofensine (3.48 g, 10.8 mmol, 1 eq) was dissolved in dry 1,2-dichloroethane (0.3 M) at 0 °C. Proton sponge (2.31 g, 10.8 mmol, 1 eq) was added, followed by 1-chloroethyl chloroformate (2.33 mL, 21.6 mmol, 2 eq). The solution was stirred at 0 °C for 15 min before being refluxed for 3 hours. After that, the solution was concentrated *in vacuo*, filtered through a silica plug, and rinsed with 100 mL 1:1:1 hexane/EtOAc/DCM. The yellow solution was concentrated *in vacuo*, dissolved in methanol (0.3 M) and refluxed for 3 hours. The solution was then concentrated *in vacuo* and neutralized using sat. $NaHCO_3$ (20 mL). The aqueous layer was extracted with EtOAc (2 x 10 mL), the combined organics were dried under Na_2SO_3 and concentrated *in vacuo*. Part of the resulting yellow oil (710 mg, 2.3 mmol, 1 eq) was dissolved in DCM (0.3 M). Triethylamine (705 µL, 5.1 mmol, 2.2 eq), DMAP (28 mg, 0.23 mmol, 0.1 eq) and phenylsulfonyl chloride (590 µL, 4.6 mmol, 2 eq) were added respectively. The solution was stirred for 12 hours before being quenched with sat. $NaHCO_3$ (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL). The combined organics were dried under Na_2SO_3 and concentrated *in vacuo*. The resulting brown oil by flash chromatography (100 mL silica, DCM loaded, gradient elution 300 mL 0% →10% → 15% → 20% EtOAc/Hex) to afford the desired product as a yellow solid in 93% yield (959 mg, 2.14 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.74 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.94 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.37 (d, *J* = 15.1 Hz, 1H), 4.30 (d, *J* = 15.1 Hz,

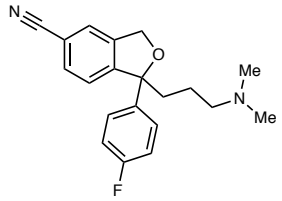
1H), 4.17 (t, *J* = 5.8 Hz, 1H), 3.77 (s, 3H), 3.61 (dd, *J* = 12.0, 4.9 Hz, 1H), 3.22 (dd, *J* = 12.0, 6.6 Hz, 1H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

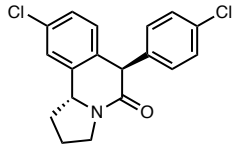
δ 158.68, 143.36, 136.43, 133.21, 133.08, 132.62, 131.20, 130.75, 130.69, 130.59, 129.25, 128.29, 127.73, 127.02, 114.04, 110.90, 55.44, 50.93, 47.99, 43.76.

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{22}H_{20}Cl_2NO_3S$ $[M+H]^+$: 448.0541, found 448.0532.



1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile [S36]
Purchased from Sigma Aldrich as the hydrobromide salt.



***rel*-(6*R*,10b*R*)-9-chloro-6-(4-chlorophenyl)-2,3,6,10b-tetrahydropyrrolo[2,1-*a*]isoquinolin-5(1*H*)-one [S37]** According to literature[19], in a 100-mL round-bottom flask were added 2-(3-chlorophenyl)pyrrolidine (910 mg, 5.01 mmol, 1.0 equiv.), 4-chloromandelic acid (934 mg, 5.01 mmol, 1.0 equiv.), and xylene (15 mL). A Dean-Stark trap and reflux condenser were placed on top of the flask. The reaction was refluxed for 40 h, and the solvent was removed in vacuo. PPA (7.5 mL) was then added to the flask, and the flask was placed into a 100 °C oil bath and heated for 1.5 h. Upon completion, water (25 mL) was added and the aqueous layer was extracted with CH_2Cl_2 3x. The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flask chromatography (75 mL silica, 300 mL 30% EtOAc/Hex) followed by medium-pressure liquid chromatography (40 g silica, 60 column volumes 0%→40% EtOAc/Hex) afforded the product as a light yellow foam (170 mg, 0.51 mmol, 10% yield). Stereochemistry was assigned by ^{1}H NMR, COSY, and NOESY 1D methods.

^{1}H NMR: (500 MHz, $CDCl_3$)

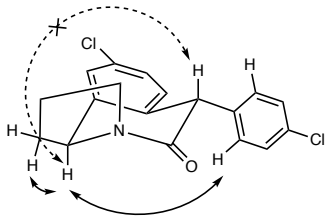
δ 7.34 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.28 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 4.84 (s, 1H), 4.47 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.65 – 3.50 (m, 2H), 2.63-2.57 (m, 1H), 2.19 – 2.09 (m, 1H), 2.00 – 1.86 (m, 2H)

^{13}C NMR: (126 MHz, $CDCl_3$)

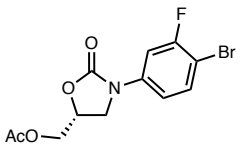
δ 167.85, 138.84, 136.06, 133.95, 133.64, 133.43, 130.00, 128.97, 128.74, 128.60, 125.01, 58.77, 53.24, 45.49, 31.71, 23.06

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{18}H_{16}NOCl_2$ $[M+H]^+$: 332.0609, found 332.0604.



For COSY and NOESY see Supporting Information: Spectral Data



(*R*)-(3-(4-bromo-3-fluorophenyl)-2-oxooxazolidin-5-yl)methyl acetate [S38] In a 100-mL recovery flask were added (*R*)-3-(4-bromo-3-fluorophenyl)-5-(hydroxymethyl)oxazolidin-2-one (Aldrich, 1.00 g, 3.45 mmol, 1.0 equiv.), DMAP (42 mg, 0.345 mmol, 0.1 equiv.), CH_2Cl_2 (20 mL), Et_3N (2.4 mL, 1.74 g, 17.2 mmol, 5 equiv.), and Ac_2O (978 µL, 1.06 g, 10.4 mmol, 3.0 equiv.). The reaction was stirred overnight, and partitioned between sat. $NaHCO_3$ and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 3x. The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flask chromatography (55 mL silica, 300 mL 50% EtOAc/Hex) afforded the product as a white solid (1.10 g, 3.33 mmol, 97% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.56 – 7.53 (m, 1H), 7.53-7.50 (m, 1H), 7.16 (ddt, *J* = 8.9, 2.3, 1.1 Hz, 1H), 4.89 (dddd, *J* = 8.8, 6.2, 4.9, 3.9 Hz, 1H), 4.38 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.31 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.10 (t, *J* = 9.0 Hz, 1H), 3.80 (dd, *J* = 8.9, 6.3 Hz, 1H), 2.10 (s, 3H).

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.62, 159.35 (d, *J* = 246.6 Hz), 153.79, 138.80 (d, *J* = 9.7 Hz), 133.73 (d, *J* = 1.8 Hz), 114.46 (d, *J* = 3.4 Hz), 106.86 (d, *J* = 27.9 Hz), 103.64 (d, *J* = 21.1 Hz), 70.16, 64.02, 47.00, 20.78

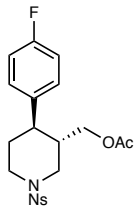
^{19}F NMR: (470 MHz, $CDCl_3$)

δ -104.51 (dd, *J* = 10.9, 7.4 Hz)

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{12}H_{12}NO_4FBr$ $[M+H]^+$: 331.9934, found 331.9943.

$[\alpha]_D^{24}$ = -48.2º (c = 0.91, CH_2Cl_2)



((3*S*,4*R*)-4-(4-fluorophenyl)-1-((4-nitrophenyl)sulfonyl)piperidin-3-yl)methyl acetate [S39] ((3*S*,4*R*)-4-(4-fluorophenyl)piperidin-3-yl)methanol (210 mg, 1.0 mmol, 1 eq) was dissolved in DCM (4 mL, 0.25 M). DMAP (12 mg, 0.10 mmol, 0.10 eq) and nosyl chloride (243 mg, 1.10 mmol, 1.1 eq) were added respectively. Triethylamine (153 µL, 1.10 mmol, 1.1 eq) was added last and the solution was stirred for 12 hours before being diluted with $NaHCO_3$ (15 mL). The aqueous layer was extracted three times with DCM (3x10 mL), and the combined organics were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting oil was dissolved in DCM (4 mL, 0.4 M), and DMAP (12 mg, 0.10 mmol, 0.1 eq), acetic anhydride (473 µL, 5.00 mmol, 5 eq), and triethylamine (418 µL, 3.00 mmol, 3 eq) were added in that order. The solution was stirred overnight before being diluted with 1M NaOH (10 mL) and DCM (10 mL). The aqueous layer was extracted with DCM (3x10 mL), and the combined organics were dried with Na_2SO_3 and concentrated *in vacuo*. The resulting crude was purified by flash chromatography (75 mL silica, dry loaded, gradient elution 300 mL 5% → 10% → 15% → 20% → 25% → 30% EtOAc/Hex) to afford the desired product as a pale white powder (349.1 mg, 0.800 mmol, 80% yield).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.42 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.07 (ddd, *J* = 8.2, 5.3, 2.5 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.09 (dt, *J* = 10.3, 2.6 Hz, 1H), 3.98 (dt, *J* = 11.1, 2.7 Hz, 1H), 3.82 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.58 (dd, *J* = 11.6, 7.0 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.33 – 2.17 (m, 3H), 2.00 (s, 3H), 1.94 – 1.84 (m, 2H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 170.80, 162.01 (d, *J* = 245.7 Hz), 150.42, 142.40, 137.59 (d, *J* = 3.3 Hz), 128.96, 128.72 (d, *J* = 7.9 Hz), 124.59, 116.02 (d, *J* = 21.3 Hz), 64.34, 49.50, 46.78, 43.86, 40.98, 33.71, 20.92.

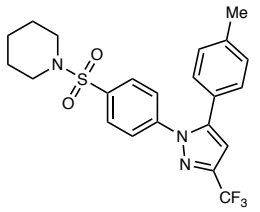
^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -115.14 (tt, *J* = 8.0, 5.2 Hz).

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{20}H_{21}FN_2NaO_6S$ $[M+Na]^+$: 459.1002, found 459.1005.

$[\alpha]_D^{24}$ = -52.9 (c = 1.00, EtOH)



1-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)piperidine [S40] Celecoxib (1.53g, 4.00 mmol, 1 eq) and K_2CO_3 (553 mg, 4 mmol, 1 eq) were dissolved in acetone (10 mL, 0.4 M). 1,5 dibromopentane (544 µL, 4 mmol, 1 eq) was added. The solution was refluxed for 3 hours after which another equivalent of K_2CO_3 was added. The solution was refluxed overnight. The solution was then concentrated *in vacuo*, diluted with EtOAc (15 mL) and 1M NaOH (10 mL). The aqueous layer was extracted with EtOAc (3x10 mL), and the combined organics were dried with Na_2SO_3 and concentrated *in vacuo*. The crude product was purified by flash chromatography (175 mL silica, dry loaded, gradient elution 300 mL 0% → 2.5 L 10% EtOAc/Hex) to afford the desired product as a white solid in 72% yield (1.29 g, 2.86 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 2.98 (t, *J* = 5.5 Hz, 4H), 2.38 (s, 3H), 1.63 (p, *J* = 5.7 Hz, 4H), 1.43 (p, *J* = 5.6, 5.1 Hz, 2H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

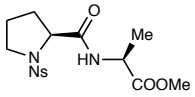
δ 145.41, 144.22 (q, *J* = 38.6 Hz), 142.57, 139.92, 136.19, 129.84, 128.81, 128.71, 125.75, 125.60, 121.17 (q, *J* = 269.1 Hz), 106.27 (d, *J* = 2.0 Hz), 47.03, 25.23, 23.59, 21.43

^{19}F NMR: (470 MHz, Chloroform-*d*)

δ -62.45

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{22}H_{23}F_3N_3O_2S$ $[M+H]^+$: 450.1463, found 450.1456.



methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-alaninate [S41] In a 500-mL round-bottom flask were added ((4-nitrophenyl)sulfonyl)-*L*-proline[5] (4.53 g, 15.1 mmol, 1 equiv.), *L*-alanine methyl ester hydrochloride (2.11 g, 15.1 mmol, 1 equiv.), and CH_2Cl_2 (160 mL). The mixture was cooled to 0 °C, and DIPEA (2.63 mL, 1.95 g, 15.1 mmol, 1 equiv.) was added dropwise, followed by HOBt (80 wt%, 2.81 g, 16.6 mmol, 1.1 equiv.) and EDC (2.34 g, 15.1 mmol, 1 equiv.). The mixture was then taken out of the ice

bath and stirred overnight, and washed with 10% citric acid, brine, and sat. $NaHCO_3$. The organic layer was dried over $MgSO_4$ and condensed in vacuo. Purification by medium-pressure liquid chromatography (40 g silica, 15 column volumes 0%→5%→10 column volumes 5% MeOH/CH_2Cl_2) afforded the product as a pale yellow powder (2.62 g, 6.81 mmol, 45% yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.55 (p, *J* = 7.2 Hz, 1H), 4.19 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.78 (s, 3H), 3.58 (ddd, *J* = 10.8, 7.4, 3.4 Hz, 1H), 3.27 (td, *J* = 9.4, 6.6 Hz, 1H), 2.27-2.19 (m, 1H), 1.94-1.81 (m, 1H), 1.81-1.67 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H)

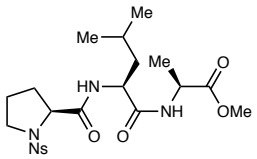
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 172.94, 170.23, 150.63, 142.53, 129.21, 124.66, 62.47, 52.76, 49.86, 48.56, 30.37, 24.71, 18.48

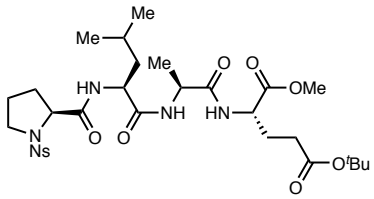
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{15}H_{20}N_3O_7S$ $[M+H]^+$: 386.1022, found 386.1020.

$[\alpha]_D^{24}$ = -120.9º (c = 1.15, CH_2Cl_2)



methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-leucyl-*L*-alaninate [S42] Prepared according to the general procedure for peptide couplings as reported in literature and the NMR data matched those reported[5].



5-(*tert*-butyl) 1-methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-leucyl-*L*-alanyl-*L*-glutamate [S43] Prepared according to the general procedure for peptide couplings as reported in literature[5].

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.47 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 4.58 – 4.50 (m, 2H), 4.46 (ddd, *J* = 9.9, 7.7, 4.4 Hz, 1H), 4.06 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.75 (s, 3H), 3.72 (ddd, *J* = 10.5, 6.7, 4.2 Hz, 1H), 3.19 (ddd, *J* =

10.0, 8.4, 6.6 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.21 – 1.79 (m, 5H), 1.76 – 1.60 (m, 4H), 1.44 (s, 9H), 1.40 (d, J = 7.2 Hz, 3H), 1.00 (d, J = 6.3 Hz, 3H), 0.95 (d, J = 6.3 Hz, 3H)

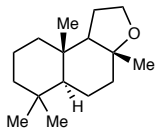
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 172.31, 172.07, 172.05, 171.44, 171.40, 150.97, 140.45, 129.63, 124.99, 80.94, 62.80, 52.88, 52.60, 51.99, 50.37, 48.97, 40.37, 31.85, 31.22, 28.23, 27.51, 25.50, 24.81, 23.25, 21.56, 17.47

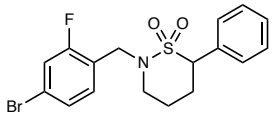
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{30}H_{46}N_5O_{11}S$ $[M+H]^+$: 684.2915, found 684.2917.

$[\alpha]_D^{24}$ = -99.8º (c = 1.22, CH_2Cl_2)



(3a*R*,5a*S*,9a*S*)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan [S44] Purchased from Sigma Aldrich.



2-(4-bromo-2-fluorobenzyl)-6-phenyl-1,2-thiazinane 1,1-dioxide [46] Prepared according to literature procedures[20].

^{1}H NMR: (500 MHz, Chloroform-*d*)

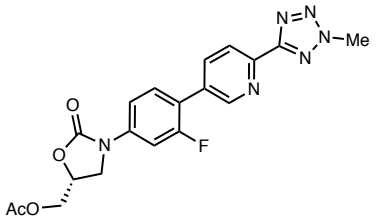
δ 7.49 – 7.45 (m, 2H), 7.44 – 7.35 (m, 4H), 7.33 (dd, J = 8.3, 1.8 Hz, 1H), 7.27 (m, 1H), 4.49 (d, J = 15.0 Hz, 1H), 4.43 (d, J = 15.0 Hz, 1H), 4.10 (dd, J = 12.9, 3.3 Hz, 1H), 3.66 (td, J = 13.6, 2.8 Hz, 1H), 3.16 (m, 1H), 2.66 (qd, J = 13.2, 3.7 Hz, 1H), 2.26 (dp, J = 13.8, 3.3 Hz, 1H), 1.92 (qt, J = 13.1, 4.0 Hz, 1H), 1.79 (dp, J = 14.4, 3.1 Hz, 1H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 160.96 (d, J = 251.0 Hz), 132.23, 132.19 (d, J = 2.2 Hz), 129.62, 129.14, 128.89, 128.08 (d, J = 3.7 Hz), 122.94 (d, J = 14.3 Hz), 122.17 (d, J = 9.5 Hz), 119.21 (d, J = 25.0 Hz), 65.05, 49.14, 44.22, 31.04, 23.04.

^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -116.28 (t, J = 8.8 Hz).



(*R*)-(3-(3-fluoro-4-(6-(2-methyl-2*H*-tetrazol-5-yl)pyridin-3-yl)phenyl)-2-oxooxazolidin-5-yl)methyl acetate [48] In a 50-mL recovery flask were added (*R*)-3-(4-bromo-3-fluorophenyl)-5-(hydroxymethyl)oxazolidin-2-one (Aldrich, 500 mg, 1.72 mmol, 1.0 equiv.), B_2Pin_2 (875 mg, 3.45 mmol, 2.0 equiv.), Pd(dppf)Cl_2•CH_2Cl_2 (70.2 mg, 0.086 mmol, 0.05 equiv.), and KOAc (677 mg, 6.90 mmol, 4.0 equiv.). The flask was backfilled with nitrogen 3x, and DMSO (5 mL) was added. The septa was quickly replaced by a yellow polyethylene cap, and the joint was secured with parafilm. The reaction was placed in 80 °C oil bath and stirred overnight. Upon completion, the reaction mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc 2x, and the organic layers were combined, washed with brine 3x, dried over $MgSO_4$, and condensed in vacuo. 5-(4-bromophenyl)-2-methyl-2*H*-tetrazole (413 mg, 1.72 mmol, 1.0 equiv.), Pd(dppf)Cl_2•CH_2Cl_2 (28.1 mg, 0.034 mmol, 0.02 equiv.), and cesium carbonate (1.68 g, 5.16 mmol, 3.0 equiv.) were added to the crude, and the flask was backfilled with nitrogen 3x. Water (2.6 mL) and dioxane (5.2 mL) were added, and the septa was quickly replaced by a polyethylene yellow cap. The reaction mixture was heated at 70 °C while stirring overnight. Upon completion, the reaction mixture was partitioned between EtOAc and water. A large amount of off-white precipitate formed and was collected through filtration. The aqueous layer was extracted with EtOAc 2x, and the organic layers were combined with the solid, and condensed in vacuo. The resulting crude was triturated 3x with EtOAc, and the remaining solid was mixed with CH_2Cl_2 (10.3 mL), DMAP (21.0 mg, 0.172 mmol, 0.1 equiv.), Et_3N (1.2 mL, 870 mg, 8.60 mmol, 5.0 equiv.), and Ac_2O (488 µL, 527 mg, 5.16 mmol, 3.0 equiv.) were added. The reaction was stirred overnight, and partitioned between CH_2Cl_2 and sat. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 3x, and the organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. Purification by flash chromatography (50 mL silica, gradient elution 300 mL 80%→600 mL 100% EtOAc/Hex) followed by twice trituration of the resulting solid with 25% EtOAc/Hex afforded the product as a pale pink powder (383 mg, 0.923 mmol, 54% overall yield).

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.94 (s, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.62 (dd, *J* = 12.7, 2.0 Hz, 1H), 7.53 (t, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.93 (dq, *J* = 9.7, 5.2 Hz, 1H), 4.47 (s, 3H), 4.42 (dd, *J* = 12.3, 3.8 Hz, 1H), 4.34 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.18 (t, *J* = 8.9 Hz, 1H), 3.88 (dd, *J* = 8.9, 6.2 Hz, 1H), 2.12 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.65, 164.87, 160.27 (d, J = 249.1 Hz), 153.87, 150.04 (d, J = 3.0 Hz), 145.72, 139.91 (d, J = 10.7 Hz), 137.22 (d, J = 3.1 Hz), 132.28, 130.82 (d, J = 4.6 Hz), 122.15, 120.61 (d, J = 13.7 Hz), 113.93 (d, J = 3.2 Hz), 106.54 (d, J = 28.4 Hz), 70.26, 64.08, 47.05, 39.90, 20.81

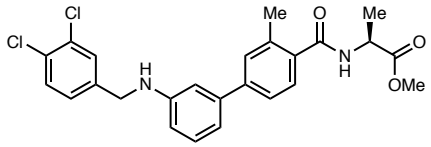
^{19}F NMR: (470 MHz, $CDCl_3$)

δ -114.34 (dd, J = 12.8, 8.3 Hz)

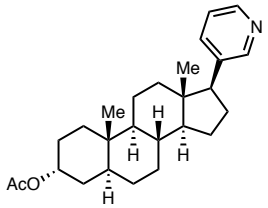
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{18}N_6O_4F$ $[M+H]^+$: 413.1374, found 413.1381.

$[\alpha]_D^{24}$ = -49.4º (c = 0.68, CH_2Cl_2)



methyl (3'-((3,4-dichlorobenzyl)amino)-3-methyl-[1,1'-biphenyl]-4-carbonyl)-*L*-alaninate [51] Prepared according to literature procedures and the NMR data matched those reported[21].

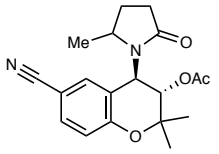


(3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-10,13-dimethyl-17-(pyridin-3-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate [(+)-53] Prepared according to literature procedures and the NMR data matched those reported[22].

VI. Experimental procedures and compound characterization for Figure 4

General procedures: In Figure 4 the general procedures for C–H oxidation, BF_3-promoted methylation, DAST-promoted methylation, and TFAA-promoted methylation were followed for all substrates unless otherwise specified.

General procedure for TFAA-promoted methylation: The crude from oxidation was dissolved in CH_2Cl_2 (1.5 mL, 0.2 M), backfilled with nitrogen 3x, and trifluoroacetic anhydride (41.7 μL, 63.0 mg, 0.30 mmol, 1.0 equiv.) was added. The reaction was stirred at room temperature for 1 h, and then placed into a -78 °C dry ice/acetone bath. Trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) and trimethylsilyl triflate (TMSOTf) (54.5 μL, 66.7 mg, 0.30 mmol, 1.0 equiv.) were then added dropwise. The reaction mixture was stirred at -78 °C for 2 h, then allowed to warm to room temperature while stirring for 1 h. Upon completion, the reaction was diluted with CH_2Cl_2 (5 mL) and poured into a 60 mL separatory funnel containing 3 mL 1 M NaOH for quenching. The aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and condensed in vacuo before subjecting to purification via flash or medium pressure chromatography.



***rel*-(3*S*,4*R*)-6-cyano-2,2-dimethyl-4-(2-methyl-5-oxopyrrolidin-1-yl)chroman-3-yl acetate [(±)-27]**
According to the general oxidation and DAST-promoted methylation procedures, *rel*-(3*S*,4*R*)-6-cyano-2,2-dimethyl-4-(2-oxopyrrolidin-1-yl)chroman-3-yl acetate **S30** (65.7 mg, 0.20 mmol, 1.0 equiv.) in MeCN (0.4 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.0075 equiv.), AcOH (172 μL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (57.7 μL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M). For facile product isolation, the oxidized products were isolated following oxidation by flash chromatography (dry loading, 50 mL silica, gradient elution 200 mL 20%→30%→50% EtOAc/$CHCl_3$), and methylated with DAST (26.4 μL, 32.2 mg, 0.20 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 300 μL, 0.60 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, 300 mL 60% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers.

Run 1 (34.9 mg, 0.102 mmol, 51% yield, 1.6:1 dr; 18.0 mg, 0.0548 mmol, 27% rsm)

Run 2 (36.6 mg, 0.107 mmol, 53% yield, 2:1 dr; 21.7 mg, 0.0661 mmol, 33% rsm)

Run 3 (25.9 mg, 0.0756 mmol, 50% yield, 1.7:1 dr; 16.7 mg, 0.0508 mmol, 34% rsm) [0.15 mmol scale]

Average overall yield: 51% (31% rsm) ± 1.5, 1.8:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

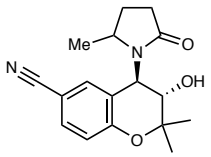
δ 7.50-7.40 (m, 1.36H), 7.23 (s, 0.64H), 6.94 (d, *J* = 8.5 Hz, 0.64H), 6.88 (d, *J* = 9.0 Hz, 0.36H), 5.70-5.16 (br m, 2H), 3.94 (sxt, *J* = 6.5 Hz, 0.36H), 3.56 (sxt, *J* = 6.5 Hz, 0.64H), 2.56 (ddd, *J* = 17.1, 10.0, 5.0 Hz, 0.36H), 2.51-2.39 (m, 1.28H), 2.34 (ddd, *J* = 17.3, 9.6, 8.2 Hz, 0.36H), 2.22-2.13 (m, 1H), 2.11 (s, 1.92H), 2.09 (s, 1.08H), 1.68-1.52 (m, 1H), 1.42 (s, 1.08H), 1.40 (s, 1.92H), 1.29 (m, 3H), 1.18 (br s, 1.92H), 0.73 (br d, *J* = 4.8 Hz, 1.08H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 177.10, 176.55, 170.34, 170.10, 157.06, 156.20, 133.10, 132.07, 123.98, 120.93, 119.27, 118.95, 118.87, 118.71, 104.73, 104.72, 79.10, 78.84, 72.38, 69.24, 53.56, 53.03, 50.24, 49.32, 30.38, 30.30, 27.92, 27.74, 26.48, 26.44, 21.93, 21.06, 21.02, 20.60, 19.35, 19.26

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{23}N_2O_4$ $[M+H]^+$: 343.1658, found 343.1666.



***rel*-(3*S*,4*R*)-3-hydroxy-2,2-dimethyl-4-(2-methyl-5-oxopyrrolidin-1-yl)chromane-6-carbonitrile [(±)-28]** In a 25-mL round-bottom flask containing *rel*-(3*S*,4*R*)-6-cyano-2,2-dimethyl-4-(2-methyl-5-oxopyrrolidin-1-yl)chroman-3-yl acetate **(±)-27** (38.1 mg, 0.102 mmol, 1.0 equiv.) was added 1 M NaOH in methanol (1 mL, 1 mmol, 10 equiv.). The reaction mixture was stirred for 1 h at room temperature and partitioned between water and CH_2Cl_2 (5 mL each). The aqueous layer was extracted with CH_2Cl_2 (3x5 mL). The organic layers were combined, dried over $MgSO_4$, condensed in vacuo, and purified by flash chromatography (20 mL silica, 200 mL 80% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers (26.1 mg, 0.0869 mmol, 85% yield, 1.5:1 dr).

Characterization of major diastereomer:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.47 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 5.52-5.14 (br s, 1H), 3.99-3.80 (br s, 1H), 3.80-3.63 (br s, 1H), 3.63-3.40 (br s, 1H), 2.70-2.40 (br m, 2H), 2.31 (dq, *J* = 15.6, 7.7 Hz, 1H), 1.74 (td, *J* = 13.0, 5.8 Hz), 1.51 (s, 3H), 1.25 (s, 3H), 1.13 (br s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 178.79, 157.69, 133.18, 131.96, 120.44, 119.26, 119.10, 104.22, 80.93, 74.62, 53.10, 30.27, 27.87, 26.67, 21.56, 18.11

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{21}N_2O_3S$ $[M+H]^+$: 301.1552, found 301.1554.

Characterization of minor diastereomer:

^{1}H NMR: (500 MHz, $CDCl_3$)

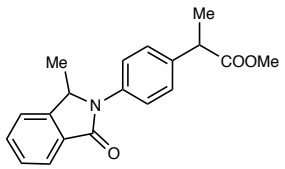
δ 7.41 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.39 (t, *J* = 1.5 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 3.98 (m, 2H), 3.23 (br s, 1H), 2.61 (ddd, *J* = 17.2, 9.6, 4.7 Hz, 1H), 2.47 (ddd, *J* = 17.3, 9.8, 8.2 Hz, 1H), 2.31 (dddd, *J* = 12.5, 9.8, 7.4, 4.8 Hz, 1H), 1.73-1.65 (m, 1H), 1.56 (s, 3H), 1.25 (s, 3H), 0.85 (d, *J* = 6.3 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 177.95, 156.55, 132.94, 132.58, 123.94, 119.22, 118.64, 104.07, 80.48, 69.21, 53.41, 51.78, 30.56, 27.51, 26.85, 22.25, 18.50

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{21}N_2O_3$ $[M+H]^+$: 301.1552, found 301.1555.



methyl 2-(4-(1-methyl-3-oxoisoindolin-2-yl)phenyl)propanoate [29] According to the general oxidation and DAST-promoted methylation procedures, methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoate **S31** (59.0 mg, 0.20 mmol, 1.0 equiv.) in 4:1 MeCN/CH_2Cl_2 (0.4 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (5.4 mg, 0.004 mmol, 0.02 equiv.), AcOH (172 μL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (57.7 μL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M), and methylated with DAST (26.4 μL, 32.2 mg, 0.20 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 300 μL, 0.60 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, 300 mL 60% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers. The starting material was resubjected once to the oxidation and methylation conditions and the products were combined.

Run 1 (1st cycle: 14.2 mg, 0.0459 mmol, 23% yield, 1:1 dr; 28.3 mg, 0.0958 mmol, 48% rsm. 2nd cycle: 6.4 mg, 0.0207 mmol, 22% yield, 1:1 dr; 16.3 mg, 0.0552 mmol, 58% rsm. Overall: 20.6 mg, 0.0666 mmol, 33% yield, 1:1 dr; 16.3 mg, 0.0552 mmol, 28% rsm)

Run 2 (1st cycle: 13.0 mg, 0.0420 mmol, 21% yield, 1:1 dr; 37.3 mg, 0.126 mmol, 63% rsm. 2nd cycle: 8.2 mg, 0.0265 mmol, 21% yield, 1:1 dr; 19.2 mg, 0.0650 mmol, 51% rsm. Overall: 21.2 mg, 0.0685 mmol, 34% yield, 1:1 dr; 19.2 mg, 0.0650 mmol, 33% rsm)

Run 3 (1st cycle: 10.3 mg, 0.0333 mmol, 17% yield, 1:1 dr; 39.7 mg, 0.134 mmol, 67% rsm. 2nd cycle: 8.9 mg, 0.0288 mmol, 22% yield, 1:1 dr; 19.5 mg, 0.0660 mmol, 49% rsm. Overall: 18.9 mg, 0.0611 mmol, 31% yield, 1:1 dr; 19.5 mg, 0.0660 mmol, 33% rsm)

Average overall yield: 33% (31% rsm) ± 1.5, 1:1 dr

Oxidative methylation with (*S*,*S*)-Mn(CF_3PDP) (0.10 equiv.): 7% yield, 16% rsm by ^{1}H NMR.

^{1}H NMR: (500 MHz, $CDCl_3$)

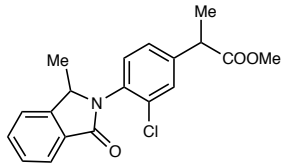
δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 5.19 (q, *J* = 6.7 Hz, 1H), 3.75 (app qd, *J* = 7.1, 2.6 Hz, 1H), 3.68 (app d, *J* = 2.7 Hz, 3H), 1.52 (app dd, *J* = 7.2, 4.8 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 175.04, 167.05, 146.38, 137.59, 137.54, 136.19, 132.23, 131.86, 128.55, 128.38, 128.35, 124.29, 123.55, 122.10, 57.00, 52.24, 45.10, 45.08, 18.96, 18.71

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{20}NO_3$ $[M+H]^+$: 310.1443, found 310.1446.



methyl 2-(3-chloro-4-(1-methyl-3-oxoisoindolin-2-yl)phenyl)propanoate [30] According to the general oxidation and DAST-promoted methylation procedures, methyl 2-(3-chloro-4-(1-oxoisoindolin-2-yl)phenyl)propanoate **S32** (66.0 mg, 0.20 mmol, 1.0 equiv.) in 4:1 MeCN/CH_2Cl_2 (0.4 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (5.4 mg, 0.004 mmol, 0.02 equiv.), AcOH (172 μL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (57.7 μL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M), and methylated with DAST (26.4 μL, 32.2 mg, 0.20 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 300 μL, 0.60 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, 300 mL 60% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers.

Run 1 (35.5 mg, 0.103 mmol, 52% yield, 1:1 dr; 5.0 mg, 0.015 mmol, 8% rsm)

Run 2 (39.4 mg, 0.115 mmol, 57% yield, 1:1 dr; 6.6 mg, 0.020 mmol, 10% rsm)

Run 3 (38.3 mg, 0.112 mmol, 56% yield, 1:1 dr; 8.3 mg, 0.025 mmol, 13% rsm)

Average overall yield: 55% (10% rsm) ± 2.7, 1:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.55-7.45 (m, 3H), 7.30 (d, *J* = 2.8 Hz, 2H), 5.16-5.07 (m, 1H), 3.75 (app qd, *J* = 7.4, 2.3 Hz, 1H), 3.71 (s, 1.5H), 3.71 (s, 1.5H), 1.53 (app dd, *J* = 7.2, 2.4 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 174.27, 167.65, 147.36, 142.08, 142.05, 133.47, 132.25, 131.30, 129.92, 129.83, 128.44, 127.13, 127.06, 124.51, 122.25, 58.36, 52.46, 45.04, 18.80, 18.63

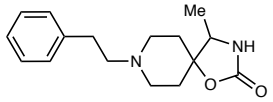
IR: (cm^{-1})

2978, 2951, 1735, 1699, 1563, 1500, 1469, 1434, 1408, 1378, 1334, 1297, 1250, 1210, 1164, 1116, 1095, 1058, 1014, 972, 888, 862, 825, 793, 758, 718, 692, 610, 538

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{19}NO_3Cl$ $[M+H]^+$: 344.1053, found 344.1048.

For HSQC and HMBC see Supporting Information: Spectral Data



4-methyl-8-phenethyl-1-oxa-3,8-diazaspiro[4.5]decan-2-one [31] Following the double-slow addition oxidation protocol and DAST-promoted procedures, fenspiride **S33** (78.9 mg, 0.303 mmol, 1.00 eq) was dissolved in DCM under N_2. HBF_4•OEt_2 (46 µL, 0.333 mmol, 1.1 eq) was added and the solution was stirred for 1 h at RT before being concentrated *in vacuo*. The resulting white solid was dissolved in 2:1 MeCN/AcOH (1.2 mL). In a 1 mL syringe, (*S*,*S*)-Mn(PDP) (28.2 mg, 0.0303 mmol, 0.1 eq) was dissolved in MeCN (0.4 mL). In a 12 mL syringe, H_2O_2 (35 µL, 0.604 mmol, 2 eq, 50 wt.% in H_2O) was dissolved in 2:1 MeCN/AcOH (3.5 mL, 0.4 M). Both syringe contents were added at 0 °C over the course of 1 h using a syringe pump. After NaOH workup to remove the HBF_4 salt, the resulting oil was purified by flash chromatography (75 mL silica, loaded with DCM, gradient elution 200 mL 4% MeOH/DCM with 1% NH_4OH → 6% MeOH/DCM with 1% NH_4OH → 8% MeOH/DCM with 1% NH_4OH → 10% MeOH/DCM with 1% NH_4OH). The RSM was isolated, and the rest of the oxidized products were combined and taken on to the methylation. The RSM was resubmitted to the HBF_4 protection, and then the oxidation conditions. Oxidized products were combined as one crude. Following oxidation, the crude was subjected to DAST (40 µL, 0.303 mmol, 1.0 eq) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 eq). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 500 mL 5% MeOH/DCM with 1% NH_4OH → 500 mL 10% MeOH/DCM with 1% NH_4OH) to afford the desired product as a pale yellow solid. To compare with the ^{1}H and ^{13}C NMR data of **S33**, we used data collected by MacMillan et al[23].

Run 1: 19.9 mg, 0.0725 mmol, 24% yield; 18.8 mg, 0.0722 mmol, 24% rsm

Run 2: 19.1 mg, 0.0696 mmol, 23% yield; 20.4 mg, 0.0784 mmol, 25% rsm

Average overall yield: 24% yield (24% rsm) ± 0.7

Lower mass balance likely resulted from aromatic oxidation.

^{1}H NMR: (500 MHz, Chloroform-*d*):

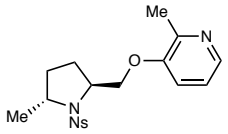
δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.32-7.17 (m, 3H), 5.42 (s, 1H), 3.61 (q, *J* = 6.5 Hz, 1H), 2.89-2.76 (m, 4H), 2.68-2.60 (m, 2H), 2.54-2.44 (m, 2H), 1.97-1.87 (m, 2H), 1.86-1.69 (m, 2H), 1.19 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 158.07, 140.27, 128.92, 128.68, 126.36, 82.66, 60.53, 56.72, 49.55, 49.37, 36.14, 33.92, 30.71, 16.35.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{16}H_{23}N_2O_2$ $[M+H]^+$: 275.1760, found 275.1756.



2-methyl-3-(((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methoxy)pyridine [32]

According to a modified general oxidation procedure and the BF_3-promoted methylation procedure, in a 40-mL vial was added (*S*)-2-methyl-3-((1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methoxy)pyridine **S34** (75.5 mg, 0.20 mmol, 1.0 equiv.), CH_2Cl_2 (0.8 mL), and HBF_4•OEt_2 (29.9 μL, 0.22 mmol, 1.1 equiv.). The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo. The crude was placed on high vacuum overnight to remove the residual acid. The crude was then redissolved in MeCN (0.4 mL, 0.5 M) and oxidized with (*S*,*S*)-Mn(CF_3PDP) (27.1 mg, 0.020 mmol, 0.10 equiv.), AcOH (172 μL, 3.00 mmol, 15.0 equiv.), and H_2O_2 (56.8 μL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M). Following oxidation, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and poured into a 60-mL separatory funnel containing 1.5 M K_2CO_3 (5 mL), and the mixture was shaken vigorously for deprotonation. The layers were seperated and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. For facile isolation, the oxidaion products were isolated by flash chromatography (50 ml silica dry loading, 200 mL 2%→5% MeOH/CH_2Cl_2), and then methylated with trimethylaluminum (2.0 M in hexanes, 300 μL, 0.60 mmol, 3.0 equiv.) and BF_3•OEt_2 (74.1 μL, 85.2 mg, 0.60 mmol, 3.0 equiv.). Following workup, the crude material was purified by medium-pressure liquid chromatography (12 g silica, 50 column volumes 0%→5%

MeOH/CH_2Cl_2) to afford the product as a white solid as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**.

Run 1 (28.2 mg, 0.0720 mmol, 36% yield; 6:1 dr; 2% rsm by ^{1}H NMR)

Run 2 (26.6 mg, 0.0680 mmol, 34% yield, 5:1 dr; 2% rsm by ^{1}H NMR)

Run 3 (25.9 mg, 0.0662 mmol, 33% yield, 6:1 dr; 2% rsm by ^{1}H NMR)

Average overall yield: 34% (2% rsm) ± 1.5, 6:1 dr

Lower mass balance was likely caused by overoxidation resulting from high catalyst loading (ca. 51% hemiaminal produced from oxidation with the rest of the material being a complex mixture).

Methylation with DAST: 28% yield, 3:1 dr by ^{1}H NMR.

^{1}H NMR: (500 MHz, $CDCl_3$)

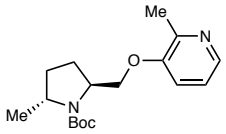
δ 8.38 (d, *J* = 8.7 Hz, 0.32H), 8.15 (d, *J* = 8.9 Hz, 1.68H), 8.11 (d, *J* = 4.5 Hz, 0.16H), 8.09-8.02 (m, 1.16H), 7.96 (d, *J* = 8.8 Hz, 1.68H), 7.18 (d, *J* = 8.0 Hz, 0.16H), 7.12 (dd, *J* = 8.2, 4.8 Hz, 0.16H), 7.05 (dd, *J* = 8.1, 4.8 Hz, 0.84H), 6.95 (d, *J* = 8.1 Hz, 0.84H), 4.33-4.18 (m, 1.84H), 4.13 (dd, *J* = 9.8, 2.6 Hz, 0.84H), 4.05 (dd, *J* = 9.8, 6.0 Hz, 0.84H), 4.02-3.93 (m, 0.32H), 3.72 (sxt, *J* = 6.3 Hz, 0.16H), 2.46 (s, 0.48H), 2.41-2.31 (m, 0.84H), 2.29 (s, 2.52H), 2.28-2.20 (m, 0.84H), 2.11 (dd, *J* = 12.9, 7.1 Hz, 0.84H), 2.08-1.99 (m, 0.16H), 1.80-1.71 (m, 0.48H), 1.65 (dd, *J* = 12.1, 6.8 Hz, 0.84H), 1.42 (d, *J* = 6.3 Hz, 0.48H), 1.29 (d, *J* = 6.4 Hz, 2.52H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 152.69, 152.26, 150.35, 149.64, 148.77, 148.32, 147.70, 143.35, 141.16, 141.11, 128.83, 127.91, 124.57, 124.22, 121.93, 121.78, 117.55, 116.83, 70.15, 68.34, 60.45, 59.21, 58.43, 58.03, 32.26, 31.95, 27.58, 27.51, 22.94, 21.67, 19.82, 19.72

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{18}H_{22}N_3O_5S$ $[M+H]^+$: 392.1280, found 392.1272.



***tert*-butyl (2*R*,5*S*)-2-methyl-5-(((2-methylpyridin-3-yl)oxy)methyl)pyrrolidine-1-carboxylate [33]**

According to literature[5], in a 25-mL recovery flask was added 2-methyl-3-(((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidin-2-yl)methoxy)pyridine **32** as a mixture of diastereomers (15.8 mg, 0.0404 mmol, 1.0 equiv.), MeCN (1.5 mL), and cesium carbonate (52.7 mg, 0.162 mmol, 4.0 equiv.). The flask was backfilled with nitrogen 3x, and DMSO (30 μL) and thiophenol (14.5 μL, 15.6 mg, 0.141 mmol, 3.5 equiv.) were added. The flask was placed in 45 °C oil bath and stirred vigorously overnight. Upon

completion, the crude was partitioned between CH_2Cl_2 and sat. $NaHCO_3$ (5 mL each), and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over K_2CO_3, condensed in vacuo, and purified through flask chromatography (20 mL alumina Brockman III, 150 mL 25% EtOAc/Hex→100 mL 5% MeOH/CH_2Cl_2) to generate the free amine as a mixture with some side products. The product was redissolved in CH_2Cl_2 (1 mL), and Boc_2O (9.7 mg, 0.0444 mmol, 1.1 equiv.) was added. The reaction was stirred overnight, and directly purified through medium-pressure liquid chromatography (12 g silica, 50 column volumes 0%→5% MeOH/CH_2Cl_2) to afford the product as a colorless oil as a mixture of diastereomers and rotamers (7.0 mg, 0.023 mmol, 57% yield, 5:1 dr).

^{1}H NMR: (500 MHz, $CDCl_3$)

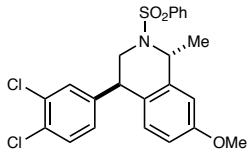
δ 8.13-8.02 (br s, 1H), 7.25-7.10 (m, 1H), 7.10-7.03 (m, 1H), 4.26-3.74 (m, 4H), 2.49 (s, 0.5H), 2.47 (s, 2.5H), 2.28-1.95 (m, 3H), 1.61-1.53 (m, 1H), 1.47 (s, 9H), 1.25 (d, J = 6.3 Hz, 0.5H), 1.23-1.15 (br s, 2.5H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 154.39, 153.66, 153.25, 153.14, 149.11, 148.76, 140.76, 140.41, 121.96, 121.73, 117.81, 117.49, 79.85, 79.59, 68.09, 67.23, 56.01, 55.98, 53.85, 53.77, 30.85, 29.76, 28.75, 28.69, 26.50, 25.66, 20.48, 19.85, 19.70, 19.52

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{17}H_{27}N_2O_3$ $[M+H]^+$: 307.2022, found 307.2022.



***rel*-(1*R*,4*R*)-4-(3,4-dichlorophenyl)-7-methoxy-1-methyl-2-(phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline [(±)-34]** Following the general oxidation and BF_3-promoted procedures, phenylsulfonyl-diclofensine **S35** (135.4 mg, 0.302 mmol, 1.00 eq) in 4:1 MeCN/DCM (1 mL, 0.3 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (8.2 mg, 0.0060 mmol, 0.02 eq), acetic acid (259 µL, 4.53 mmol, 15.0 eq), and H_2O_2 (26 µL, 0.604 mmol, 2 eq, 50 wt.% in H_2O) in 4:1 MeCN/DCM (3.5 mL, 0.4 M) at -36 °C via single addition protocol. After 30 min, another 8.2 mg of the catalyst in 0.4 mL MeCN was added to the reaction. Following oxidation, the crude was methylated with BF_3 (75 µL, 0.60 mmol, 2.0 eq) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 eq). Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 30 CV 0% to 12.5%, 5 CV 12.5%, 10 CV 12.5% to 30% EtOAc/Hex) to produce the desired compound as a white powder.

Run 1: 34.9 mg, 0.0755 mmol, 25% yield, >20:1 dr; 22% rsm by ^{1}H NMR

Run 2: 32.1 mg, 0.0695 mmol, 23% yield, >20:1 dr; 22% rsm by ^{1}H NMR

Run 3: 30.7 mg, 0.0664 mmol, 22% yield, >20:1 dr; 27% rsm by ^{1}H NMR

Average overall yield: 23% yield (24% rsm) ± 1.2

Lower mass balance is likely a result of aromatic oxidation.

^{1}H NMR: (500 MHz, Chloroform-*d*)

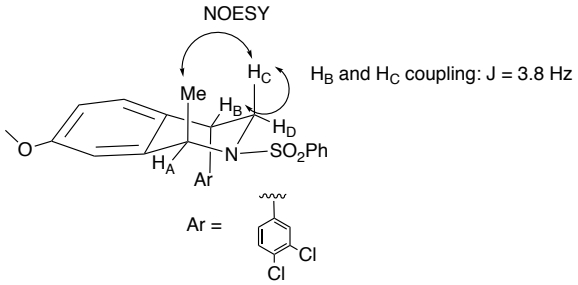
δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.72 (s, 2H), 6.61 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.23 (q, *J* = 6.7 Hz, 1H), 4.03 (dd, *J* = 4.0, 1.9 Hz, 1H), 3.84 (s, 3H), 3.79 (dd, *J* = 13.4, 3.8 Hz, 1H), 3.71 (dd, *J* = 13.3, 2.0 Hz, 1H), 1.60 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

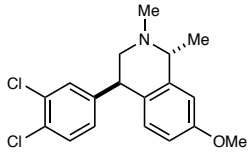
δ 158.79, 144.42, 139.94, 139.74, 132.34, 132.18, 131.37, 130.66, 130.34, 130.12, 128.76, 127.78, 127.09, 125.24, 113.95, 111.71, 55.48, 52.59, 45.39, 42.95, 22.45.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{23}H_{22}Cl_2NO_3S$ $[M+H]^+$: 462.0697, found 462.0680.



For NOESY see Supporting Information: Spectral Data



***rel*-(1*R*,4*R*)-4-(3,4-dichlorophenyl)-7-methoxy-1,2-dimethyl-1,2,3,4-tetrahydroisoquinoline [35]** *rel*-(1*R*,4*R*)-4-(3,4-dichlorophenyl)-7-methoxy-1-methyl-2-(phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline **34** (46.2 mg, 0.1 mmol, 1 eq), magnesium turnings (243.1 mg, 10 mmol, 100 eq), and NH_4Cl (534.9 mg, 10 mmol, 100 eq) were dissolved in methanol (5.3 mL). The reaction was sonicated at rt for 1 hour. The solution was passed through a celite plug, rinsed with DCM, and diluted with $NaHCO_3$. The aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na_2SO_3), concentrated *in vacuo*, and the resulting oil was dissolved in DCM (2 mL). Formaldehyde (37%, 180µL, 2.2 mmol, 22 eq) and formic acid (190 µL, 5.0 mmol, 50 eq) was added and the solution was stirred at 90 °C for 12 hours. The solution was then transferred to a separatory funnel with 10 mL 1M NaOH, and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na_2SO_3)

and concentrated *in vacuo*. The resulting oil was purified via column chromatography (30 mL silica, DCM loaded, 100 mL 0% → 5% MeOH/DCM with 1% NH_4OH) and furnished the desired product in 82% yield (27.6 mg, 0.82 mmol) as a transparent oil.

^{1}H NMR: (500 MHz, Chloroform-*d*)

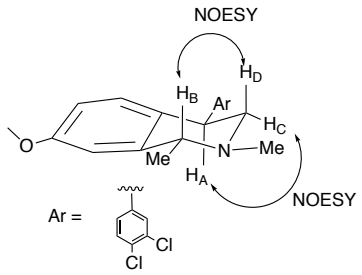
δ 7.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.27-7.25 (m, 1H), 7.01 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.16 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.79 (s, 3H), 3.77 – 3.70 (m, 1H), 3.13 (dd, *J* = 11.7, 5.0 Hz, 1H), 2.59 (dd, *J* = 11.7, 8.7 Hz, 1H), 2.46 (s, 3H), 1.45 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

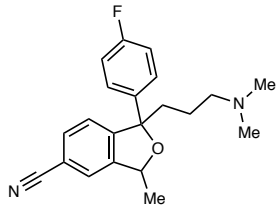
δ 158.24, 145.32, 132.42, 130.88, 130.56, 130.41, 130.33, 130.11, 128.70, 128.50, 112.19, 111.85, 59.76, 59.08, 55.39, 29.85, 18.85.

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{18}H_{20}Cl_2NO$ [$M+H_3O^+$]: 336.0922, found 336.0925.



For NOESY see Supporting Information: Spectral Data



1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-3-methyl-1,3-dihydroisobenzofuran-5-carbonitrile

[36] Following the general oxidation and DAST-promoted procedures, citalopram **S36** (98.0 mg, 0.302 mmol, 1.00 eq) was dissolved in DCM under N_2. HBF_4•OEt_2 (46 µL, 0.332 mmol, 1.1 eq) was added and the solution was stirred for 1 h at RT before being concentrated *in vacuo*. The resulting white solid was dissolved in MeCN (1 mL, 0.3 M). Acetic acid (259 µL, 4.53 mmol, 15.0 eq) was added. In a 1 mL syringe, (*S*,*S*)-Mn(CF_3PDP) (40.7 mg, 0.0303 mmol, 0.1 eq) was dissolved in MeCN (0.4 mL). In a 12 mL syringe, H_2O_2 (34 µL, 0.604 mmol, 2 eq, 50 wt.% in H_2O) was dissolved in MeCN (3.5 mL, 0.4 M). Both syringe contents were added over the course of 1 hr using a syringe pump at -36 °C. After NaOH workup to remove the HBF_4 salt, the resulting oil was purified by flash chromatography (50 mL

Brockman grade III Al_2O_3, loaded with DCM, gradient elution 200 mL 90% EtOAc/hex → 200 mL 2% MeOH/DCM with 1% NH_4OH → 5% → 10% MeOH/DCM with 1% NH_4OH) to afford the oxidized products as a pale yellow foam. The mixture was subjected to DAST (40 µL, 0.303 mmol, 1.0 eq) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 eq). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 50% → 70% EtOAc/Hex → 5% MeOH/DCM with 1% NH_4OH → 7% MeOH/DCM with 1% NH_4OH → 10% MeOH/DCM with 1% NH_4OH) to afford the desired product as a pale yellow oil.

Run 1: 38.1 mg, 0.113 mmol, 37% yield, 1:1 dr; 12% rsm by ^{1}H NMR

Run 2: 36.9 mg, 0.109 mmol, 36% yield, 1:1 dr; 9% rsm by ^{1}H NMR

Run 3: 35.8 mg, 0.106 mmol, 34% yield, 1:1 dr; 14% rsm by ^{1}H NMR

Average overall yield: 36% yield (12% rsm) ± 1.5

Lower mass balance is likely the result of aromatic (fluorinated phenyl) oxidation caused by the high catalyst loading.

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.58 – 7.51 (m, 0.9H), 7.50 – 7.45 (m, 1H), 7.46 – 7.41 (m, 2.1H), 7.40 – 7.29 (m, 4.4H), 7.23 – 7.13 (m, 1H), 6.97 – 6.90 (m, 3.8H), 5.39 (q, *J* = 6.4 Hz, 1H), 5.20 (q, *J* = 6.3 Hz, 0.9H), 2.27 – 1.98 (m, 18.3H), 1.52 (app t, *J* = 6.4 Hz, 5.5H), 1.41 (m, 2.2H), 1.31 – 1.20 (m, 2.5H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

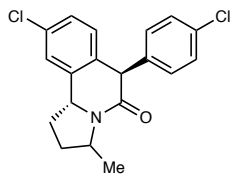
δ 162.09 (d, *J* = 246.2 Hz), 162.04 (d, *J* = 246.1 Hz), 149.85, 149.45, 144.88, 144.20, 140.40 (d, *J* = 3.3 Hz), 139.88 (d, *J* = 3.2 Hz), 132.04, 132.00, 127.14 (d, *J* = 8.1 Hz), 126.78 (d, *J* = 7.9 Hz), 125.27, 125.25, 123.02, 122.81, 118.78, 118.76, 115.33 (d, *J* = 21.4 Hz), 115.32 (d, *J* = 21.6 Hz), 111.91, 111.88, 90.43, 90.12, 78.67, 77.31, 59.47, 59.45, 45.35, 39.56, 39.12, 22.36, 22.26, 21.15.

^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -114.53 (dtd, *J* = 17.2, 8.7, 4.4 Hz), -115.59 (dtd, *J* = 17.6, 8.4, 4.2 Hz).

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{21}H_{24}FN_2O$ $[M+H]^+$: 339.1873, found 339.1866.



***rel*-(6*R*,10b*R*)-9-chloro-6-(4-chlorophenyl)-3-methyl-2,3,6,10b-tetrahydropyrrolo[2,1-*a*]isoquinolin-5(1*H*)-one [(±)-37]** According to the general oxidation and DAST-promoted methylation procedures, *rel*-

(6*R*,10b*R*)-9-chloro-6-(4-chlorophenyl)-2,3,6,10b-tetrahydropyrrolo[2,1-*a*]isoquinolin-5(1*H*)-one **(±)-S37** (33.2 mg, 0.10 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.17 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.7 mg, 0.002 mmol, 0.02 equiv.), AcOH (86 μL, 1.50 mmol, 15.0 equiv.), and H_2O_2 (28.4 μL, 0.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (1.25 mL, 0.4 M), and methylated with DAST (13.2 μL, 16.1 mg, 0.10 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 150 μL, 0.30 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, 200 mL 20%→30%→50% EtOAc/Hex) to afford the product as a colorless oil as a mixture of diastereomers.

Run 1 (14.1 mg, 0.0407 mmol, 41% yield, 4:1 dr; 11.4 mg, 0.0343 mmol, 34% rsm)

Run 2 (14.2 mg, 0.0410 mmol, 41% yield, 4:1 dr; 14.5 mg, 0.0436 mmol, 44% rsm)

Run 3 (16.8 mg, 0.0485 mmol, 49% yield, 4:1 dr; 12.2 mg, 0.0367 mmol, 37% rsm)

Average overall yield: 44% (38% rsm) ± 4.6, 4:1 dr

^{1}H NMR: (500 MHz, $CDCl_3$)

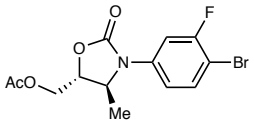
δ 7.36 (d, *J* = 8.0 Hz, 0.8H), 7.32 (d, *J* = 8.0 Hz, 0.2H), 7.28-7.26 (m, 0.8H), 7.26-7.24 (m, 0.2H), 7.24-7.20 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 0.8H), 7.15 (d, *J* = 8.0 Hz, 0.2H), 7.03 (d, *J* =8.6 Hz, 2H), 4.84 (s, 0.8H), 4.76 (s, 0.2H), 4.53 (dd, *J* = 10.7, 5.9 Hz, 0.2H), 4.38 (dd, *J* = 11.0, 5.9 Hz, 0.8H), 4.26-4.14 (m, 1H), 2.53 (dd, *J* = 12.2, 6.2 Hz, 0.2H), 2.48-2.38 (m, 0.8H), 2.30 (dt, *J* = 13.7, 7.3 Hz, 0.2H), 2.18-2.03 (m, 1.6H), 1.89-1.71 (m, 1H), 1.63-1.54 (m, 0.2H), 1.31 (d, *J* = 6.2 Hz, 0.6H), 1.23 (d, *J* = 6.3 Hz, 2.4H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 168.02, 167.54, 139.75, 138.45, 136.98, 135.13, 134.70, 133.65, 133.55, 133.40, 133.28, 129.33, 129.89, 128.98, 128.91, 128.77, 128.57, 128.45, 125.21, 124.43, 59.13, 58.70, 53.95, 53.77, 53.40, 53.21, 32.01, 31.62, 31.14, 28.28, 19.99, 19.62

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{19}H_{18}NOCl_2$ $[M+H]^+$: 346.0765, found 346.0751.



((4*S*,5*R*)-3-(4-bromo-3-fluorophenyl)-4-methyl-2-oxooxazolidin-5-yl)methyl acetate [38] According to the general oxidation and TFAA-promoted methylation procedures, (*R*)-(3-(4-bromo-3-fluorophenyl)-2-oxooxazolidin-5-yl)methyl acetate **S38** (99.6 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (8.1 mg, 0.0060 mmol, 0.02 equiv.), AcOH (257 μL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M).

Following oxidation, the crude was methylated with TFAA (41.7 μL, 63.0 mg, 0.30 mmol, 1.0 equiv.), trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.), and TMSOTf (54.5 μL, 66.7 mg, 0.30 mmol, 1.0 equiv.). Following workup, the crude material was purified by medium-pressure liquid chromatography (12 g silica, 50 column volumes 0%→50% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers. The stereochemistry was determined by ^{1}H NMR and NOESY 1D methods.

Run 1 (46.8 mg, 0.135 mmol, 45% yield; 6:1 dr; 38.9 mg, 0.117 mmol, 39% rsm)

Run 2 (45.0 mg, 0.130 mmol, 43% yield, 7:1 dr; 36.9 mg, 0.111 mmol, 37% rsm)

Run 3 (46.0 mg, 0.133 mmol, 44% yield, 5:1 dr; 33.1 mg, 0.100 mmol, 33% rsm)

Average overall yield: 44% (36% rsm) ± 1.0, 6:1 dr

Methylation with DAST:

Run 1 (31.7 mg, 0.0916 mmol, 31% yield, 11:1 dr; 7.6 mg, 0.020 mmol, 6% hemiaminal acetate; 41.1 mg, 0.124 mmol, 41% rsm)

Run 2 (32.2 mg, 0.0930 mmol, 31% yield, 12:1 dr; 10.0 mg, 0.0256 mmol, 9% hemiaminal acetate; 42.5 mg, 0.128 mmol, 43% rsm)

Average overall yield: 31% (42% rsm) ± 0.0, 12:1 dr; 8% hemiaminal acetate

Gram scale: Following the general oxidation and TFAA-promoted procedures, (*R*)-(3-(4-bromo-3-fluorophenyl)-2-oxooxazolidin-5-yl)methyl acetate (1.00 g, 3.02 mmol, 1.0 equiv.) in MeCN (7 mL) in a 100 mL round-bottom flask was oxidized with (S,S)-Mn(CF_3PDP) (81.6 mg, 0.0604 mmol, 0.02 equiv.), acetic acid (2.59 mL, 45.3 mmol, 15.0 equiv.), and H_2O_2 (855 μL, 15.1 mmol, 5.0 equiv., 50 wt.% in H_2O) in MeCN (37.5 mL, in 50 mL HSW syringe). Following oxidation, the solution was passed through 100 mL silica and flushed with 1 L of EtOAc. The solution was concentrated *in vacuo* and transferred to a 100 mL round bottom flask and left on a high vacuum pump overnight. The crude was then dissolved in 40 mL of CH_2Cl_2 under nitrogen. TFAA (418 μL, 3.02 mmol, 1.0 equiv.) was added and the solution was stirred for an hour. Subsequently, the solution was cooled to -78°C and $AlMe_3$ (4.52 mL, 9.06 mmol, 3.0 equiv.) was added dropwise along the side of the flask. TMSOTf (545 μL, 3.02 mmol, 1 eq) was then added dropwise, and the reaction was stirred at -78°C for an hour before removing the dry ice bath and stirring at rt for 3 hours. A 3 M solution of sodium hydroxide (100 mL) was cooled to 0 °C at the end of the reaction and transferred to a 250 mL separatory funnel. The reaction mixture was cooled to 0 °C and slowly transferred to the separatory funnel. The organic layer was carefully extracted, and the aqueous layer was washed with EtOAc (3 x 30 mL). The combined organic layers were dried with Na_2SO_4,

concentrated *in vacuo*, and purified via MPLC (40 g silica, 60 column volumes 0%→30% EtOAC/Hex) to afford the desired product as a white solid as a mixture of diastereomers.

Run 1 (463 mg, 1.34 mmol, 44% yield, 4:1 dr; 369.7 mg, 1.11 mmol, 37% rsm)

Run 2 (482 mg, 1.39 mmol, 46% yield, 4:1 dr; 358.1 mg, 1.08 mmol, 36% rsm)

Average overall yield: 45% (37% rsm), 4:1 dr

Characterization of major diastereomer **38**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 10.4, 2.5 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.39 (q, *J* = 4.7 Hz, 1H), 4.36-4.27 (m, 2H), 4.24 (p, *J* = 6.0 Hz, 1H), 2.08 (s, 3H), 1.40 (d, *J* = 6.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.62, 159.37 (d, *J* = 247.1 Hz), 154.01, 137.30 (d, *J* = 9.3 Hz), 133.78 (d, *J* = 1.5 Hz), 117.43 (d, *J* = 3.4 Hz), 109.71 (d, *J* = 26.8 Hz), 104.67 (d, *J* = 21.1 Hz), 77.64, 63.57, 54.19, 20.74, 18.60

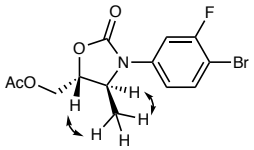
^{19}F NMR: (470 MHz, $CDCl_3$)

δ -104.50 (dd, *J* = 10.3, 7.8 Hz)

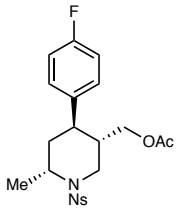
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{13}H_{14}NO_4FBr$ $[M+H]^+$: 346.0090, found 346.0088.

$[\alpha]_D^{24}$ = -44.3º (c = 1.10, CH_2Cl_2)



For NOESY see Supporting Information: Spectral Data



((3*S*,4*R*,6*R*)-4-(4-fluorophenyl)-6-methyl-1-((4-nitrophenyl)sulfonyl)piperidin-3-yl)methyl acetate [39] Following the general oxidation and BF_3-promoted methylation procedures, ((3*S*,4*R*)-4-(4-fluorophenyl)-1-((4-nitrophenyl)sulfonyl)piperidin-3-yl)methyl acetate **S39** (131.8 mg, 0.302 mmol, 1 eq) and acetic acid (259 µL, 4.53 mmol, 15.0 eq) were dissolved in MeCN (0.6 mL, 0.4 M). (*R*,*R*)-Mn(CF_3PDP) (40.9 mg, 0.03 mmol, 0.1 eq) was dissolved in MeCN (0.4 mL), and H_2O_2 (86 µL, 1.51

mmol, 5 eq, 50 wt.% in H_2O) was dissolved in MeCN (3 mL) in separate syringes. The two separate solutions of catalyst and oxidant were added over 1 hour using a syringe pump at 0 °C. Following oxidation, the crude was methylated with BF_3 (75 µL, .60 mmol, 2.0 eq) and $AlMe_3$ (2.0 M in hexanes, 450 µL, .90 mmol, 3.0 eq). Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 25 CV 0% to 15%, 3 CV 15%, 4 CV 15% to 17.5%, 5 CV 17.5% EtOAc/Hex) to produce the desired compound as a mixture with RSM.

Run 1: 47.6 mg, 0.106 mmol, 35% yield > 20:1 dr; 16% rsm by ^{1}H NMR.

Run 2: 44.9 mg, 0.100 mmol, 33% yield > 20:1 dr; 14% rsm by ^{1}H NMR.

Run 3: 46.3 mg, 0.103 mmol, 34% yield > 20:1 dr; 20% rsm by ^{1}H NMR.

Average overall yield: 34% yield (16% rsm) ± 0.8

The desired methylated product was cleanly isolated when the oxidation product was cleanly isolated. After oxidation (see above), the crude material was purified by column chromatography (50 mL silica, loaded with DCM and ethyl acetate, gradient elution 200 mL 0% → 10% → 600 mL 20% → 100% ethyl acetate/hexane). All oxidized products were collected and submitted to the methylation conditions mentioned above. Following workup, the crude material was purified by column chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 0% → 5% → 10% → 15% → 20% → 25% ethyl acetate/hexane) to produce the desired compound as a white solid in 28% yield.

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 8.39 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.04 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.42 (p, *J* = 6.3 Hz, 1H), 4.03 (dd, *J* = 13.4, 4.4 Hz, 1H), 3.82 (dd, *J* = 11.6, 3.4 Hz, 1H), 3.64 (dd, *J* = 11.6, 7.7 Hz, 1H), 2.93 (dd, *J* = 13.5, 11.5 Hz, 1H), 2.69 (td, *J* = 12.4, 3.7 Hz, 1H), 2.08-2.03 (m, 1H), 2.02 (s, 3H), 1.89 (td, *J* = 13.3, 5.3 Hz, 1H), 1.66 (ddd, *J* = 13.6, 3.8, 1.9 Hz, 1H), 1.12 (d, *J* = 6.9 Hz, 3H).

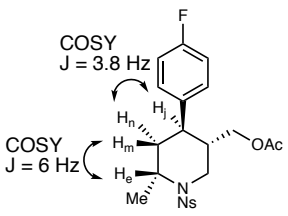
^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 170.79, 161.96 (d, *J* = 245.7 Hz), 150.10, 147.00, 137.67 (d, *J* = 3.3 Hz), 128.77 (d, *J* = 7.9 Hz), 128.28, 124.66, 115.98 (d, *J* = 21.3 Hz), 64.31, 49.05, 42.94, 41.29, 39.40, 38.25, 20.91, 15.61.

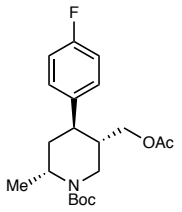
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{21}H_{24}FN_2O_6S$ $[M+H]^+$: 451.1339, found 451.1332.

$[\alpha]_D^{24}$ = -27.0 (c = 1.00, EtOH)



For COSY see Supporting Information: Spectral Data



***tert*-butyl (2*R*,4*R*,5*S*)-5-(acetoxymethyl)-4-(4-fluorophenyl)-2-methylpiperidine-1-carboxylate [40]**

((3*S*,4*R*,6*R*)-4-(4-fluorophenyl)-6-methyl-1-((4-nitrophenyl)sulfonyl)piperidin-3-yl)methyl acetate **39** (65.0 mg, 0.144 mmol, 1 eq) was dissolved in a 45:1 MeCN/DMSO solution (0.1 M). Thiophenol (52 µL, 0.504 mmol, 3.5 eq) and Cs_2CO_3 (187.2 mg, 0.58 mmol, 4 eq) were subsequently added. The reaction was stirred at 45°C overnight. The reaction was then diluted with brine (10 mL) and DCM (15 mL), and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na_2SO_3), concentrated *in vacuo*, and the resulting oil was then dissolved in DCM (5 mL). Boc_2O (157 mg, 0.792 mmol, 5 eq) was added and the reaction as stirred at rt overnight before being diluted with $NaHCO_3$ (15 mL). The aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na_2SO_3), concentrated *in vacuo*, and the resulting oil was purified by column chromatography (20 mL silica, DCM loaded, 200 mL 0% → 10 → 20% EtOAC/hex) to afford the desired product as an oil in 86% yield as a mixture of rotamers (45.2 mg, 0.124 mmol).

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.16 – 7.07 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.66 – 4.35 (m, 1H), 4.35 – 3.99 (m, 1H), 3.87-3.77 (m, 1H), 3.67 (dd, *J* = 11.3, 8.1 Hz, 1H), 2.87 – 2.51 (m, 2H), 2.02 – 1.91 (m, 4H), 1.87 (td, *J* = 13.2, 5.6 Hz, 1H), 1.70 – 1.59 (m, 1H), 1.48 (s, 9H), 1.21 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 171.03, 170.90, 161.77 (d, *J* = 244.9 Hz), 155.08, 154.60, 138.88 (d, *J* = 3.1 Hz), 128.82 (d, *J* = 7.8 Hz), 115.72 (d, *J* = 21.2 Hz), 79.81, 65.05, 64.85, 46.85, 45.65, 41.91, 41.49, 41.02, 40.94, 39.32, 39.02, 29.83, 28.60, 20.87, 16.16, 15.91.

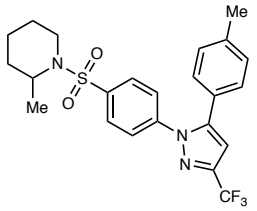
^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -116.08 (m).

HRMS: (ESI TOF MS ES+)

m/z calculated for $C_{20}H_{29}FNO_4$ [M+H$^+$]: 366.2081, found 366.2078.

$[\alpha]_D^{19}$ = -63.3° (c = 1.00, EtOH)



2-methyl-1-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)piperidine [41]

Following the general oxidation and BF_3-promoted procedures, 1-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)piperidine **S40** (271.5 mg, 0.604 mmol, 1.00 eq) in MeCN/DCM (2:0.5 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (4.1 mg, 0.003 mmol, 0.005 eq), acetic acid (518 µL, 9.06 mmol, 15.0 eq), and H_2O_2 (172 µL, 3.0 mmol, 5 eq, 50 wt.% in H_2O) in MeCN/DCM (5.6 mL:1.4 mL), at 0 °C via single addition protocol. Following workup, the crude material was purified to separate the starting material from all oxidized products via column chromatography (50 mL silica, DCM loaded, 150 mL 0% → 300 mL 10% → 20% → 100% ethyl acetate/hexane). The starting material was isolated and resubmitted to the oxidation. The combined oxidation products were submitted to the methylation with BF_3 (150 µL, 1.2 mmol, 2.0 eq) and $AlMe_3$ (2.0 M in hexanes, 900 µL, 1.8 mmol, 3.0 eq). Following workup, the crude material was purified by MPLC (40 g silica, dry loaded, gradient elution 30 CV 0% to 5%, 15 CV 5% EtOAc/Hex) to produce the desired compound as a white powder.

Run 1: 114.9 mg, 0.248 mmol, 41% yield; 20% rsm by ^{1}H NMR

Run 2: 109.6 mg, 0.236 mmol, 39% yield; 18% rsm by ^{1}H NMR

Average overall yield: 40% yield (19% rsm) ± 1.4

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 4.23 (p, *J* = 6.3 Hz, 1H), 3.71 (dt, *J* = 12.3, 3.3 Hz, 1H), 2.99 (td, *J* = 13.2, 2.6 Hz, 1H), 2.37 (s, 3H), 1.63 – 1.50 (m, 4H), 1.44 (m, 1H), 1.39 – 1.29 (m, 1H), 1.07(d, *J* = 6.93 Hz, 3H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

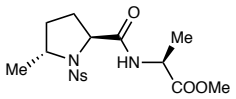
δ 145.26, 143.99 (q, *J* = 38.5 Hz), 142.01, 141.06, 139.73, 129.67, 128.70, 127.89, 125.71, 125.61, 121.08 (q, *J* = 269.2 Hz), 106.12 (d, *J* = 2.1 Hz), 48.71, 40.40, 30.30, 25.20, 21.31, 18.09, 15.49.

^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -62.40.

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{23}H_{25}F_3N_3O_2S$ $[M+H]^+$: 464.1620, found 464.1609.



Methyl ((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonyl)-*L*-alaninate [42]

According to the general oxidation and DAST-promoted methylation procedures, methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-alaninate **S41** (115.6 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (85.2 µL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). Following oxidation, the crude was methylated with DAST (39.6 µL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 20%→400 mL 30% EtOAc/Hex) to afford the product as a white solid or gel. The stereochemistry was determined based on ^{1}H NMR, COSY, and NOESY 1D NMR methods.

Run 1 (75.7 mg, 0.189 mmol, 63% yield; 6:1 dr; 3% rsm by ^{1}H NMR)

Run 2 (75.5 mg, 0.189 mmol, 63% yield, 6:1 dr; 2% rsm by ^{1}H NMR)

Run 3 (73.5 mg, 0.184 mmol, 61% yield, 6:1 dr; 6% rsm by ^{1}H NMR)

Average overall yield: 62% (4% rsm) ± 1.2, 6:1 dr

A similar yield (69.0 mg, 0.173 mmol, 58% yield; 5:1 dr; 14% rsm by ^{1}H NMR) was obtained when substituting DAST for Deoxo-Fluor (55.3 µL, 66.4 mg, 0.30 mmol, 1.0 equiv.).

Characterization for major diastereomer **42**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 6.38 (d, *J* = 7.2 Hz, 1H), 4.45 (p, *J* = 7.2 Hz, 1H), 4.40-4.36 (m, 1H), 4.07-4.00 (m, 1H), 3.75 (s, 3H), 2.32-2.20 (m, 2H), 2.11-2.00 (m, 1H), 1.66-1.58 (m, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 3H)

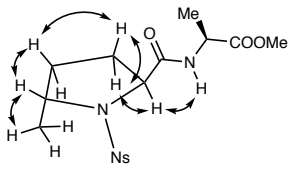
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 173.13, 170.79, 150.10, 146.04, 129.02, 124.13, 63.10, 57.21, 52.77, 48.42, 32.46, 29.09, 21.42, 18.42

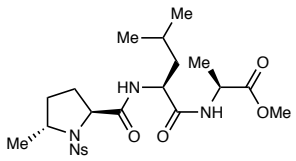
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{16}H_{22}N_3O_7S$ $[M+H]^+$: 400.1178, found 400.1180.

$[\alpha]_D^{24}$ = -102.0º (c = 0.10, CH_2Cl_2)



For COSY and NOESY see Supporting Information: Spectral Data



methyl ((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonyl)-*L*-leucyl-*L*-alaninate [43] According to the general oxidation and DAST-promoted methylation procedures, methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-leucyl-*L*-alaninate **S42** (149.6 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (85.2 µL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). For facile product isolation, the oxidized products were isolated following oxidation by flash chromatography (dry loading, 50 mL silica, gradient elution 200 mL 20%→30%→40%→100% EtOAc/$CHCl_3$). The starting material was resubjected 1x to the oxidation conditions, and the oxidized products were combined. The combined hemiaminal was then methylated with DAST (39.6 µL, 48.3 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 500 mL 50%→200 mL 75% EtOAc/Hex) to afford the product as a white solid as a mixture of diastereomers. The stereochemistry was determined by analogy to compounds **13** and **42**.

Run 1 (93.4 mg, 0.182 mmol, 61% yield, 6:1 dr; 31.3 mg, 0.0628 mmol, 21% rsm)

Run 2 (86.8 mg, 0.169 mmol, 56% yield, 8:1 dr; 33.9 mg, 0.0680 mmol, 23% rsm)

Average overall yield: 59% (22% rsm) ± 3.5, 7:1 dr

Methylation with BF_3•OEt_2: trace yield, 18% rsm by ^{1}H NMR.

Characterization for major diastereomer **43**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.43 (d, *J* = 8.5 Hz, 1H), 4.54 (p, *J* = 7.3 Hz, 1H), 4.47 (td, *J* = 9.4, 4.8 Hz, 1H), 4.32 (d, *J* = 8.6 Hz, 1H), 4.24 (p, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 2.26 (tdd, *J* = 12.0, 8.7, 6.1 Hz, 1H), 2.17 (dq, *J* = 12.0, 5.6, 4.8 Hz, 1H), 2.13-2.06 (m, 1H), 1.82 (ddd, *J* = 13.8, 8.8, 4.8 Hz, 1H), 1.68-1.54 (m, 3H), 1.37 (d, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H)

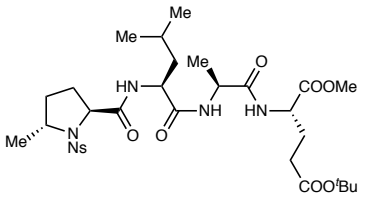
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 173.20, 171.25, 171.20, 150.31, 145.31, 129.19, 124.40, 62.96, 57.99, 52.55, 52.12, 48.22, 41.01, 32.18, 29.55, 25.18, 23.26, 21.74, 20.46, 18.16

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{22}H_{33}N_4O_8S$ $[M+H]^+$: 513.2019, found 513.2025.

$[\alpha]_D^{24}$ = -101.9º (c = 0.87, CH_2Cl_2)



5-(*Tert*-butyl) 1-methyl ((2*S*,5*R*)-5-methyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carbonyl)-*L*-leucyl-*L*-alanyl-*L*-glutamate [44] According to the general oxidation and fluorination-promoted methylation procedures, 5-(*tert*-butyl) 1-methyl ((4-nitrophenyl)sulfonyl)-*L*-prolyl-*L*-leucyl-*L*-alanyl-*L*-glutamate **S43** (205.1 mg, 0.30 mmol, 1.0 equiv.) in MeCN (0.6 mL, 0.5 M) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 equiv.), AcOH (257 µL, 4.50 mmol, 15.0 equiv.), and H_2O_2 (85.2 µL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). For facile product isolation, the oxidized products were isolated following oxidation by flash chromatography (dry loading, 50 mL silica, gradient elution 200 mL 50%→60%→400 mL 70% EtOAc/Hex), and methylated with Deoxo-Fluor (55.3 µL, 66.4 mg, 0.30 mmol, 1.0 equiv.) and trimethylaluminum (2.0 M in hexanes, 450 µL, 0.90 mmol, 3.0 equiv.). Following workup, the crude material was purified by flash chromatography (50 mL silica, gradient elution 200 mL 20%→400 mL 30% EtOAc/Hex) to afford the product as a white solid. The starting material was then resubjected once to the oxidation and methylation conditions. The stereochemistry was determined by analogy to compounds **13** and **42**.

Run 1 (1st cycle: 81.3 mg, 0.117 mmol, 39% yield, 6:1 dr; 75.2 mg, 0.110 mmol, 37% rsm. 2nd cycle: 26.8 mg, 0.0384 mmol, 35% yield, 4:1 dr; 37.1 mg, 0.0543 mmol, 49% rsm. Overall: 108.1 mg, 0.155 mmol, 52% yield, 5:1 dr; 37.1 mg, 0.0543 mmol, 18% rsm)

Run 2 (1st cycle: 71.4 mg, 0.102 mmol, 34% yield, 5:1 dr; 97.7 mg, 0.143 mmol, 48% rsm. 2nd cycle: 31.8 mg, 0.0456 mmol, 32% yield, 5:1 dr; 52.6 mg, 0.0769 mmol, 54% rsm. Overall: 103.2 mg, 0.148 mmol, 49% yield, 5:1 dr; 52.6 mg, 0.0769 mmol, 26% rsm)

Run 3 (1st cycle: 80.6 mg, 0.115 mmol, 38% yield, 6:1 dr; 113.2 mg, 0.166 mmol, 55% rsm. 2nd cycle: 27.2 mg, 0.0390 mmol, 29% yield, 4:1 dr; 49.6 mg, 0.0725 mmol, 55% rsm. Overall: 107.8 mg, 0.154 mmol, 51% yield, 5:1 dr; 49.6 mg, 0.0725 mmol, 24% rsm)

Average overall yield: 51% (23% rsm) ± 1.5, 5:1 dr

Characterization for major diastereomer **44**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.41 (d, *J* = 8.3 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 1H), 4.52 (app p, *J* = 7.4 Hz, 2H), 4.45-4.36 (m, 2H), 4.33 (p, *J* =

6.6 Hz, 1H), 3.74 (s, 3H), 2.42-2.23 (m, 3H), 2.21-2.07 (m, 3H), 2.07-1.96 (m, 1H), 1.91-1.80 (m, 1H), 1.73-1.59 (m, 3H), 1.45 (s, 9H), 1.35 (d, J = 7.1 Hz, 3H), 1.11 (d, J = 6.4 Hz, 3H), 1.10 (d, J = 6.0 Hz, 3H), 0.95 (d, J = 6.1 Hz, 3H)

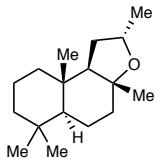
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 172.37, 172.10, 172.07, 171.43, 150.49, 145.47, 129.21, 124.70, 80.97, 63.07, 58.07, 53.02, 52.59, 51.98, 48.93, 40.52, 32.23, 31.92, 29.55, 28.25, 27.50, 25.47, 23.30, 21.51, 19.95, 17.56

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{31}H_{48}N_5O_{11}S$ $[M+H]^+$: 698.3071, found 698.3071.

$[\alpha]_D^{24}$ = -73.0º (c = 0.38, CH_2Cl_2)



(2*S*,3a*R*,5a*S*,9a*S*,9b*R*)-2,3a,6,6,9a-pentamethyldodeca-hydronaphtho[2,1-*b*]furan [45] Following the general oxidation and DAST-promoted methylation protocols, (–)-Ambroxide **S44** (71.5 mg, 0.302 mmol, 1 eq) in 4:1 MeCN/DCM (1.25 mL) was oxidized with (*S*,*S*)-Mn(CF_3PDP) (2.0 mg, 0.0015 mmol, 0.005 eq), acetic acid (259 µL, 4.53 mmol, 15 eq), and H_2O_2 (34 µL, 0.604 mmol, 2 eq) in 4:1 MeCN/DCM (3.5 mL, 0.4 M), at -36 °C via single addition protocol. Following oxidation, the crude mixture was methylated with DAST (40 µL, 0.302 mmol, 1 eq) and $AlMe_3$ (450 µL, 0.90 mmol, 3 eq). Following workup, the resulting oil was purified using liquid chromatography (50 mL silica, loaded with DCM, 300 mL 0% → 0.5% → 1% → 1.5% → 2% → 4% EtOAc/Hex) to afford the desired products. The major was isolated, while the minor was only recovered as a mixture with the major and the rsm. The stereochemistry was assigned by matching with the ^{1}H NMR data reported in the literature[24].

Run 1: 24.3 mg, 0.0970 mmol, 32% yield, 3:1 dr; 27% rsm by ^{1}H NMR

Run 2: 26.8 mg, 0.107 mmol, 35% yield, 3:1 dr; 21% rsm by ^{1}H NMR.

Run 3: 21.2 mg, 0.0846 mmol, 28% yield, 3:1 dr; 24% rsm by ^{1}H NMR.

Average overall yield: 32% yield (24% rsm) ± 2.9, 3:1 dr.

19% of lactone product (sclareolide) was also isolated.

Characterization of major diastereomer **45**:

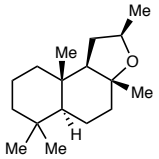
^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 4.21 (dqd, J = 8.9, 6.3, 2.7 Hz, 1H), 1.96 – 1.84 (m, 2H), 1.73 (dq, J = 13.9, 3.2 Hz, 1H), 1.70 – 1.59 (m, 1H), 1.51 – 1.35 (m, 5H), 1.29 (ddt, J = 14.4, 10.4, 3.2 Hz, 2H), 1.18-1.13 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H), 1.11 (s, 3H), 1.06 – 0.94 (m, 2H), 0.87 (s, 3H), 0.82 (s, 6H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 81.29, 71.77, 59.13, 57.47, 42.64, 40.28, 40.07, 36.21, 33.74, 33.25, 30.02, 23.38, 21.68, 21.30, 20.73, 18.58, 15.11.

$[\alpha]_D^{22}$ = -34.3 (c = 1.00, EtOH)



Characterization of minor diastereomer **S45**:

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 4.08 (dp, *J* = 8.8, 6.3 Hz, 1H), 1.92 (dt, *J* = 11.4, 3.2 Hz, 1H), 1.88 – 1.79 (m, 1H), 1.73 (dq, *J* = 13.9, 3.2 Hz, 1H), 1.70 – 1.60 (m, 1H), 1.53 (dd, *J* = 13.5, 5.2 Hz, 1H), 1.48 – 1.34 (m, 4H), 1.32-1.23 (m, 2H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.18 (dd, *J* = 13.8, 4.6 Hz, 1H), 1.13 (d, *J* = 0.9 Hz, 3H), 1.04 (dd, *J* = 12.9, 3.8 Hz, 1H), 0.95 (dd, *J* = 12.4, 2.8 Hz, 1H), 0.86 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H).

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 80.48, 74.58, 61.69, 57.28, 42.65, 40.69, 40.22, 36.41, 33.70, 33.27, 31.16, 25.10, 23.88, 21.24, 20.97, 18.61, 15.75.

HRMS: (ESI TOF MS ES+)

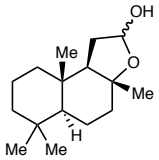
m/z calculated for $C_{17}H_{31}O$ $[M+H]^+$: 251.2375, found 251.2380.

Oxidation of **S44** using 10 mol% **1** and 5 equiv. H_2O_2:

Run 1: 24.2 mg, 0.0966 mmol, 32% sclareolide; 1.8 mg, 0.006 mmol, 2% hemiacetal acetate.

Run 2: 26.0 mg, 0.103 mmol, 34% sclareolide; 0.9 mg, 0.003 mmol, 1% hemiacetal acetate.

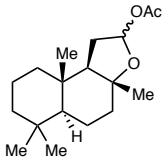
Average yield: 0% hemiacetal (0% rsm); 2% hemiacetal acetate; 33% sclareolide



Characterization of hemiacetal intermediate (NOTE: exists as an equilibrium with the open form of the hemiacetal which is the aldehyde):

^{1}H NMR: (500 MHz, Chloroform-*d*)

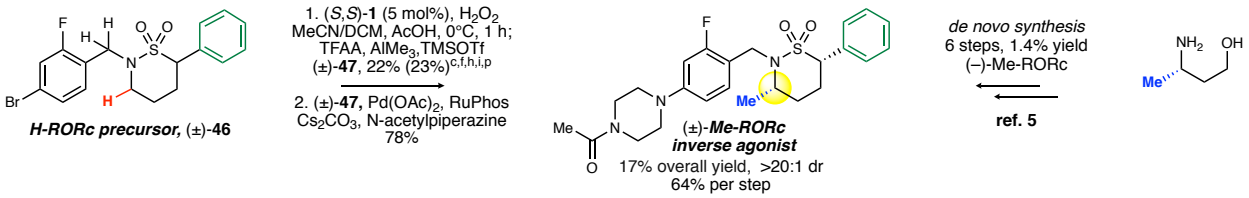
δ 9.75 (s, 0.2H), 5.57 – 5.20 (m, 1H), 3.08-2.80 (m, 0.5 H), 2.67 – 2.27 (m, 0.2H), 2.01 – 1.87 (m, 1.8H), 1.74 – 1.59 (m, 4H), 1.47 – 1.34 (m, 4.8H), 1.34 – 1.09 (m, 7H), 1.07 – 0.90 (m, 2H), 0.89 – 0.78 (m, 12H).

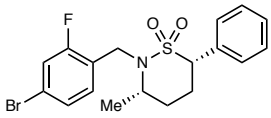


Characterization of hemiacetal acetate intermediate (NOTE: not very stable to column conditions, can revert back to the hemiaminal)

^{1}H NMR: (400 MHz, Chloroform-*d*)

δ 6.25-6.17 (m, 1H), 2.23-2.08 (m, 1H), 2.05 (s, 3H), 2.02-1.88 (m, 1H), 1.88-1.59 (m, 3H), 1.55-1.36 (m, 4H), 1.36-1.15 (m, 2H), 1.26 (s, 3H), 1.16-0.90 (m, 3H), 0.88 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H)





2-(4-bromo-2-fluorobenzyl)-cis-3-methyl-6-phenyl-1,2-thiazinane 1,1-dioxide [(±)-47] Following the general oxidation and TMSOTf-promoted procedures, 2-(4-bromo-2-fluorobenzyl)-6-phenyl-1,2-thiazinane 1,1-dioxide **46** (120.3 mg, 0.302 mmol, 1.00 eq) in MeCN/DCM (1.2/0.3 mL) was oxidized with (*S*,*S*)-Mn(CF$_3$PDP) (20.5 mg, 0.015 mmol, 0.05 eq), acetic acid (259 µL, 4.53 mmol, 15 eq), and H_2O_2 (86 µL, 1.51 mmol, 5 eq, 50 wt.% in H_2O) in MeCN (3.75 mL) at 0 °C via single addition protocol. Following oxidation plug, the mixture was purified via column chromatography to isolate the starting material from the oxidized products (50 mL silica, DCM loaded, 200 mL 0% → 5% → 15% EtOAc/hex). The starting material was resubmitted to the oxidation, and the oxidized products from both runs were combined and submitted to methylation with TFAA (43 µL, 0.302 mmol, 1.0 eq), TMSOTf (109 µL, 0.604 mmol, 2.0 eq) and AlMe$_3$ (2.0 M in hexanes, 453 µL, 0.906 mmol, 3.0 eq). Following workup, the crude material was purified by flash chromatography (50 mL silica, loaded with DCM, gradient elution 200 mL 0% → 2% → 4 % → 6% → 8% → 10% → 20% EtOAc/Hex) to afford the product as a white solid.

Run 1: 24.9 mg, 0.0604 mmol, 20% yield; 23% rsm and > 20:1 dr by ^{1}H NMR.

Run 2: 31.1 mg, 0.0755 mmol, 25% yield; 22% rsm and > 20:1 dr by ^{1}H NMR.

Run 3: 27.4 mg, 0.0664 mmol, 22% yield; 23% rsm and > 20:1 dr by ^{1}H NMR.

Average overall yield: 22% yield (23% rsm) ± 2.5, >20:1 dr.

Lower mass balance likely resulted from aromatic oxidation.

^{1}H NMR: (500 MHz, Chloroform-*d*)

δ 7.50 – 7.46 (m, 2H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.29 – 7.22 (m, 1H), 4.60 (d, *J* = 15.3 Hz, 1H), 4.39 (d, *J* = 15.4 Hz, 1H), 4.07 (dd, *J* = 12.5, 3.3 Hz, 1H), 3.59 (qt, *J* = 7.1, 3.6 Hz, 1H), 2.90 (dtd, *J* = 15.8, 13.1, 3.1 Hz, 1H), 2.26 – 2.12 (m, 1H), 2.05 (tdd, *J* = 13.6, 5.5, 3.6 Hz, 1H), 1.75 (m, 1H), 1.49 (d, *J* = 7.1 Hz, 3H)

^{13}C NMR: (126 MHz, Chloroform-*d*)

δ 160.91 (d, *J* = 250.7 Hz), 132.33, 131.96 (d, *J* = 4.6 Hz), 129.71, 129.11, 128.83, 128.05 (d, *J* = 3.7 Hz), 123.83 (d, *J* = 14.3 Hz), 121.93 (d, *J* = 9.5 Hz), 119.19 (d, *J* = 25.1 Hz), 65.79, 55.70, 44.08 (d, *J* = 3.4 Hz), 29.60, 26.48, 17.40

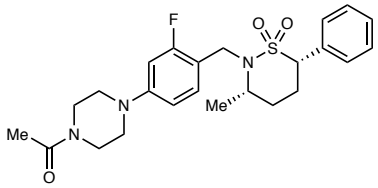
^{19}F NMR: (471 MHz, Chloroform-*d*)

δ -116.50 (t, *J* = 8.7 Hz)

HRMS: (ESI TOF MS ES+)

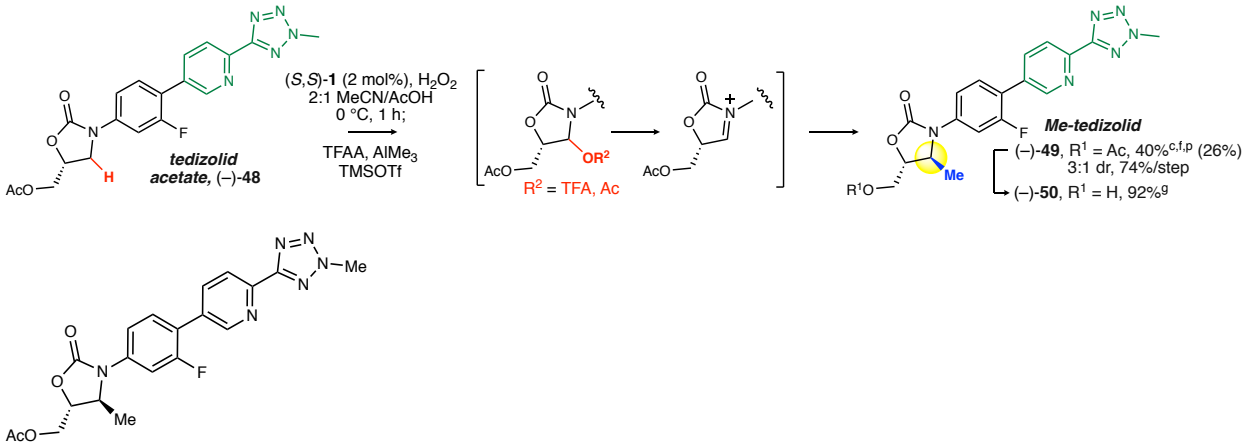
m/z calculated for $C_{18}H_{20}BrFNO_2S$ $[M+H]^+$: 412.0382, found 412.0358.

Relative stereochemistry was assigned by taking the product and cross-coupling to 1-acetylpiperazine (as described in the original publication) and comparing the NMR data to the published work[5].



^{1}H NMR: (500 MHz, DMSO-d_6)

δ 7.49 – 7.43 (m, 2H), 7.43 – 7.34 (m, 3H), 7.29 (t, *J* = 8.9 Hz, 1H), 6.84 – 6.74 (m, 2H), 4.41 – 4.37 (m, 3H), 3.61 – 3.46 (m, 5H), 3.22 (t, *J* = 5.2 Hz, 2H), 3.15 (t, *J* = 5.3 Hz, 2H), 2.77 – 2.65 (m, 1H), 2.14 – 1.98 (m, 5H), 1.66 – 1.55 (m, 1H), 1.34 (d, *J* = 7.1 Hz, 3H).



((4*S*,5*R*)-3-(3-fluoro-4-(6-(2-methyl-2*H*-tetrazol-5-yl)pyridin-3-yl)phenyl)-4-methyl-2-oxooxazolidin-5-yl)methyl acetate [49] According to a modified general oxidation procedure and the TFAA-promoted methylation procedure, (*R*)-(3-(3-fluoro-4-(6-(2-methyl-2*H*-tetrazol-5-yl)pyridin-3-yl)phenyl)-2-oxooxazolidin-5-yl)methyl acetate **48** (82.5 mg, 0.20 mmol, 1.0 equiv.) and (*S*,*S*)-Mn(CF_3PDP) (5.4 mg, 0.0040 mmol, 0.02 equiv.) in a 40-mL vial were dissolved in 2:1 MeCN/AcOH (3.0 mL, 0.067 M). The reaction mixture was then placed into an ice bath at 0°C. A 10 mL syringe was charged with a solution of H_2O_2 (56.8 µL, 1.00 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (2.50 mL, 0.4 M). The syringe was then fitted with a 25G needle and the solution was slowly added into the stirring reaction mixture via a syringe pump at 2.50 mL/h. Upon completion, the vial was taken from the cold bath, and the reaction mixture was immediately loaded onto a 15 mL silica plug. Ethyl acetate was used to rinse the vial (2x1 mL), and the resulting washes were also loaded onto the silica plug. The plug was allowed to sit for five minutes in order to decompose any remaining hydrogen peroxide as well as absorbing the reaction mixture. Ethyl acetate (150 mL) was then allowed to pass through the plug and the eluent condensed. For facile isolation, the oxidation products were isolated from the crude by medium-pressure liquid chromatography (24 g silica, 50 column volumes 0%→10% MeOH/CH_2Cl_2). The crude from oxidation was dissolved in CH_2Cl_2 (1.0 mL, 0.2 M), backfilled with nitrogen 3x, and trifluoroacetic anhydride (27.8 µL, 42.0 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction was stirred at room temperature for 1 h, and then placed into a -78 °C dry ice/acetone bath. Trimethylaluminum (2.0 M in hexanes, 300 µL, 0.90 mmol, 3.0 equiv.) and TMSOTf (72.7 µL, 88.9 mg, 0.40 mmol, 2.0 equiv.) were then added dropwise. The reaction mixture was stirred at -78 °C for 2 h, then allowed to warm to room temperature while stirring for 1 h. Upon completion, the reaction was diluted with CH_2Cl_2 (5 mL) and poured into a 60 mL separatory funnel containing 3 mL 1 M NaOH for quenching. The aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and condensed in vacuo. Flash chromatography (20 mL silica, 200 mL EtOAc) afforded the product as a white solid as a mixture of diastereomers. The stereochemistry was determined by analogy to product **50**.

Run 1 (33.4 mg, 0.0783 mmol, 39% yield, 3:1 dr; 25.0 mg, 0.0606 mmol, 30% rsm)

Run 2 (33.0 mg, 0.0773 mmol, 39% yield, 3:1 dr; 22.5 mg, 0.0546 mmol, 27% rsm)

Run 3 (35.3 mg, 0.0829 mmol, 41% yield, 3:1 dr; 17.6 mg, 0.0427 mmol, 21% rsm)

Average overall yield: 40% (26% rsm) ± 1.2, 3:1 dr

Methylation with Deoxo-Fluor: 4.9 mg, 0.012 mmol, 6% yield, 5:1 dr; 10.6 mg, 0.0261 mmol, 13% hemiaminal acetate; 14.7 mg, 0.0358 mmol, 18% enamine; 16.5 mg, 0.0400 mmol, 20% rsm

Methylation of isolated hemiaminal acetate intermediate [0.026 mmol scale] with BF_3: 0% yield, 5% rsm by ^{1}H NMR

Characterization of major diastereomer **49**:

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.94 (s, 1H), 8.32 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.06 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.52 (t, *J* = 8.5 Hz, 1H), 7.46 (dd, *J* = 12.4, 2.2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.48 (s, 3H), 4.46-4.41 (m, 1H), 4.38-4.30 (m, 3H), 1.45 (d, *J* = 6.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 170.67, 164.82, 160.27 (d, *J* = 249.5 Hz), 154.09, 150.00 (d, *J* = 3.4 Hz), 145.78, 138.51 (d, *J* = 10.9 Hz), 137.33 (d, *J* = 3.8 Hz), 132.26 (d, *J* = 1.8 Hz), 130.86 (d, *J* = 4.6 Hz), 122.17, 121.44 (d, *J* = 13.8 Hz), 116.74 (d, *J* = 3.4 Hz), 109.28 (d, *J* = 27.3 Hz), 77.71, 63.66, 54.21, 39.91, 20.81, 18.79

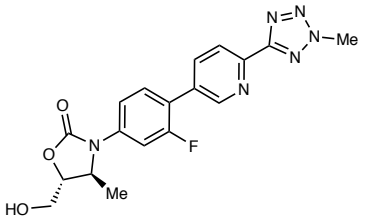
^{19}F NMR: (470 MHz, $CDCl_3$)

δ -114.90 (app t, *J* = 9.2 Hz)

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{20}H_{20}N_6O_4F$ $[M+H]^+$: 427.1530, found 427.1532.

$[\alpha]_D^{24}$ = -52.9º (c = 0.67, CH_2Cl_2)



(4*S*,5*R*)-3-(3-fluoro-4-(6-(2-methyl-2*H*-tetrazol-5-yl)pyridin-3-yl)phenyl)-5-(hydroxymethyl)-4-methyloxazolidin-2-one [50] In a 10-mL round-bottom flask containing ((4*S*,5*R*)-3-(3-fluoro-4-(6-(2-methyl-2*H*-tetrazol-5-yl)pyridin-3-yl)phenyl)-4-methyl-2-oxooxazolidin-5-yl)methyl acetate **49** as the major diastereomer (10.7 mg, 0.025 mmol, 1.0 equiv.) was added 1 M NaOH in methanol (0.25 mL, 0.25 mmol, 10 equiv.). The reaction mixture was stirred for 1 h at room temperature and directly loaded onto

column and purified by flash chromatography (20 mL silica, 200 mL 0%→100 mL 5% EtOAc/MeOH) to afford the product as a white foam (8.8 mg, 0.023 mmol, 92% yield). The stereochemistry was determined by ^{1}H NMR, COSY, and NOESY 1D methods.

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.92 (s, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 8.04 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.52 (t, *J* = 8.5 Hz, 1H), 7.49 (dd, *J* = 12.4, 2.1 Hz, 1H), 7.34 (dd, *J* = 8.9, 2.1 Hz, 1H), 4.52-4.47 (m, 1H), 4.47 (s, 3H), 4.31 (dt, *J* = 5.6, 3.7 Hz, 1H), 4.01 (d, *J* = 12.7, 3.3 Hz, 1H), 3.81 (d, *J* = 11.4 Hz, 1H), 2.26 (br s, 1H), 1.45 (d, *J* = 6.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 164.85, 160.20 (d, *J* = 249.5 Hz), 154.69, 150.02 (d, *J* = 3.0 Hz), 145.73, 138.64 (d, *J* = 10.6 Hz), 137.25 (d, *J* = 3.8 Hz), 132.31, 130.73 (d, *J* = 4.4 Hz), 122.15, 121.37 (d, *J* = 13.3 Hz), 117.07 (d, *J* = 3.4 Hz), 109.55 (d, *J* = 27.0 Hz), 80.65, 62.34, 53.21, 39.89, 18.68

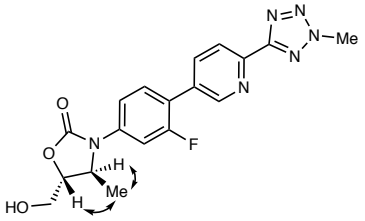
^{19}F NMR: (470 MHz, $CDCl_3$)

δ -114.67 (dd, *J* = 12.3, 8.7 Hz)

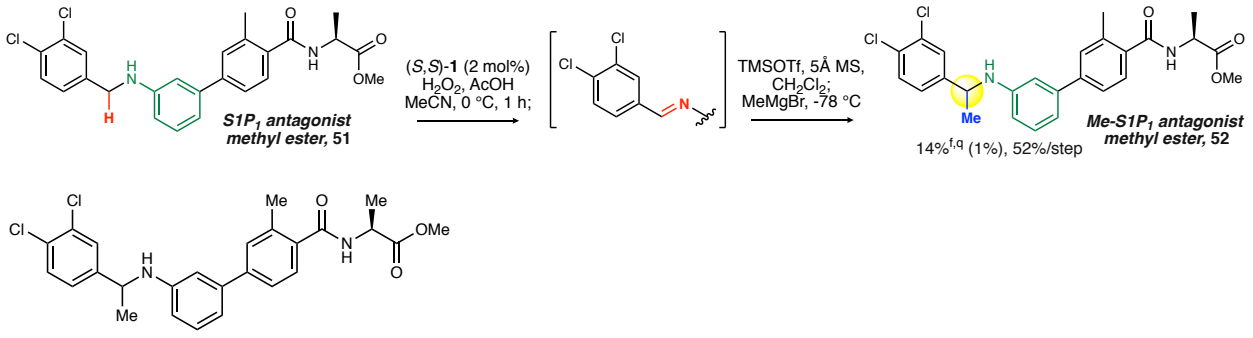
HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{18}H_{18}N_6O_3F$ $[M+H]^+$: 385.1424, found 385.1413.

$[\alpha]_D^{24}$ = -49.2° (c = 0.44, CH_2Cl_2)



For COSY and NOESY see Supporting Information: Spectral Data



Methyl (3'-((1-(3,4-dichlorophenyl)ethyl)amino)-3-methyl-[1,1'-biphenyl]-4-carbonyl)-*L*-alaninate [52] To a 40 mL vial equipped with a stir bar were added methyl (3'-((3,4-dichlorobenzyl)amino)-3-methyl-[1,1'-biphenyl]-4-carbonyl)-*L*-alaninate **51** (141.4 mg, 0.30 mmol, 1.0 equiv,), (*S*,*S*)-Mn(CF_3PDP)

(8.1 mg, 0.0060 mmol, 0.02 equiv.), MeCN (1.8 mL, 0.17 M), and AcOH (257 μL, 4.50 mmol, 15.0 equiv.). The reaction mixture was heated on 70 °C hot plate until fully dissolved, then placed into an ice bath at 0°C. A 10 mL syringe was charged with a solution of H_2O_2 (85.2 μL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in MeCN (3.75 mL, 0.4 M). The syringe was then fitted with a 25G needle and the solution was slowly added into the stirring reaction mixture via a syringe pump at 3.75 mL/h. Upon completion, the vial was taken from the cold bath, and the reaction mixture was immediately loaded onto a 15 mL silica plug. Ethyl acetate was used to rinse the vial (2x1 mL), and the resulting washes were also loaded onto the silica plug. The plug was allowed to sit for five minutes in order to decompose any remaining hydrogen peroxide as well as absorbing the reaction mixture. Ethyl acetate (150 mL) was then allowed to pass through the plug, and the eluent was concentrated in vacuo. The recovered starting material was isolated by flash chromatography (dry loading, 50 mL silica, gradient elution 400 mL 30%→500 mL 40% EtOAc/Hex). All other fractions were combined, condensed in vacuo, transferred into a 25 mL recovery flask, condensed, and placed on vacuum overnight. To the same recovery flask was then added CH_2Cl_2 (1.5 mL) and flame-dried 5 Å powdered molecular sieves (40 mg). The flask was again placed in ice bath, backfilled with N_2 3x, and TMSOTf (1.2 equiv. to crude imine) was added dropwise. The reaction was allowed to stir at 0 °C for 1 h, then placed into a -78 °C cold bath. Methylmagnesium bromide (3 M, 3.0 equiv. to crude imine) was then added, and the reaction was stirred at -78 °C for 4 h. Water (100 μL) was added to quench the reaction, which was then warmed to room temperature in a water bath. The crude was transferred to a 20 mL Erlenmeyer flask, dried over $MgSO_4$, and condensed in vacuo. It was observed by crude ^{1}H NMR that there was unreacted imine. The crude was transferred into a 25 mL recovery flask, placed on vacuum overnight, and resubjected 1x to same amounts of TMSOTf and MeMgBr. Following workup, the crude material was purified by medium-pressure liquid chromatography (12 g silica, 50 column volumes gradient elution 0%→50% EtOAc/Hex) to afford the product as a white foam.

Run 1 (18.6 mg, 0.0383 mmol, 13% yield; 16.4 mg, 0.0349 mmol, 12% recovered imine)

Run 2 (22.3 mg, 0.0459 mmol, 15% yield; 20.0 mg, 0.0426 mmol, 14% recovered imine; 1.5 mg, 0.0032 mmol, 1% rsm)

Run 3 (20.8 mg, 0.0428 mmol, 14% yield; 19.0 mg, 0.0405 mmol, 13% recovered imine; 1.5 mg, 0.0032 mmol, 1% rsm)

Average overall yield: 14% (1% rsm) ± 1.0; 13% recovered imine

Lower mass balance resulted from aromatic oxidation and hydrolysis of the imine intermediate during oxidation, which formed aldehyde product that was subsequently oxidized to carboxylic acid.

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.50 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33-7.28 (m, 2H), 7.24 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H),

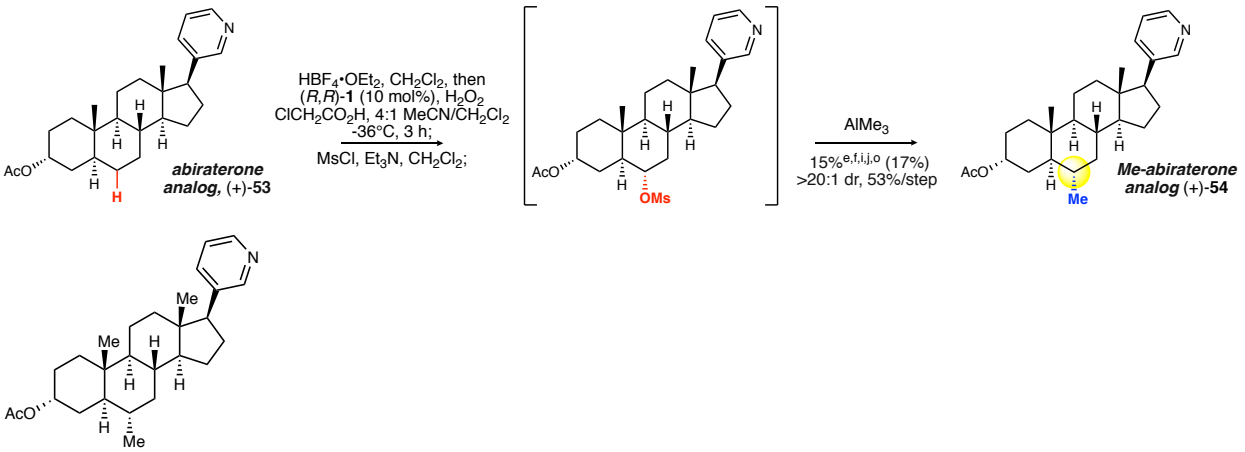
6.45 (d, J = 8.0, 2.3 Hz, 1H), 6.36 (d, J = 7.6 Hz, 1H), 4.81 (p, J = 7.2 Hz, 1H), 4.48 (q, J = 6.7 Hz, 1H), 4.14 (br s, 1H), 3.80 (s, 3H), 2.50 (s, 3H), 1.53 (d, J = 7.4 Hz, 6H)

^{13}C NMR: (126 MHz, $CDCl_3$)

δ 173.65, 169.37, 147.18, 145.82, 143.45, 141.47, 136.90, 134.48, 132.93, 130.92, 130.88, 130.00, 129.81, 128.08, 127.52, 125.43, 124.53, 117.03, 112.76, 112.46, 53.08, 52.70, 48.48, 25.10, 20.18, 18.75

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{26}H_{27}N_2O_3Cl_2$ $[M+H]^+$: 485.1399, found 485.1393.



(3*R*,5*R*,6*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-6,10,13-trimethyl-17-(pyridin-3-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate [(+)-54] According to a modified general oxidation procedure, in a 40-mL vial was added (3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-10,13-dimethyl-17-(pyridin-3-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (+)-**53** (118.7 mg, 0.30 mmol, 1.0 equiv.), CH_2Cl_2 (1.2 mL), and HBF_4•OEt_2 (44.9 µL, 0.33 mmol, 1.1 equiv.). The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo. The crude was placed on high vacuum overnight to remove the residual acid. (*R*,*R*)-Mn(CF_3PDP) (40.7 mg, 0.030 mmol, 0.10 equiv.) and $ClCH_2COOH$ (425 mg, 4.50 mmol, 15.0 equiv.) were added to the crude, and the mixture was dissolved in 4:1 MeCN/CH_2Cl_2 (1 mL, 0.3 M) and placed in a -36 °C dry ice/1,2-DCE bath. A 10 mL syringe was charged with a solution of H_2O_2 (85.2 µL, 1.50 mmol, 5.0 equiv, 50 wt.% in H_2O) in 4:1 MeCN/CH_2Cl_2 (3.75 mL, 0.4 M). The syringe was then fitted with a 25G needle and the solution was slowly added into the stirring reaction mixture over 3 h via a syringe pump at 1.25 mL/h. Following oxidation, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and cooled to 0 °C. 3 M NaOH (5 mL) was added, and the mixture was stirred vigorously for 5 min. The layers were seperated and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. For facile isolation, the alcohol product was isolated by medium-pressure liquid chromatography (12 g silica, 100 column

volumes 0%→70% EtOAc/Hex), and redissolved in CH_2Cl_2 (1 mL). MsCl (23.2 μL, 34.4 mg, 0.30 mmol, 1.0 equiv.) was added, followed by Et_3N (41.8 μL, 30.4 mg, 0.30 mmol, 1.0 equiv.). The reaction was stirred at room temperature for 1 h, then partitioned between sat. $NaHCO_3$ and CH_2Cl_2. The layers were separated and the aqueous layer was extracted wit CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo, then redissolved in CH_2Cl_2 (1 mL) and cooled to -78 °C. Trimethylaluminum (2.0 M in hexanes, 450 μL, 0.90 mmol, 3.0 equiv.) was then added, and the reaction was stirred at -78 °C for 2 h and room temperature for 1 h. Upon completion, the mixture was diluted the CH_2Cl_2 and quenched with 1 M NaOH (5 mL). The layers were separated and the aqueous layer was extracted wit CH_2Cl_2 (2x5 mL). The organic layers were combined, dried over $MgSO_4$, and condensed in vacuo. The crude material was purified by flash chromatography (20 mL silica, 200 mL 20% EtOAc/Hex) to afford the product as a white solid. Stereochemistry was assigned by ^{1}H NMR, COSY, and 1D NOESY methods on the product's deacetylated derivative **S46**.

Run 1 (16.7 mg, 0.0408 mmol, 14% yield, >20:1 dr; 11.8 mg, 0.0298 mmol, 10% rsm; 24.2 mg, 0.059 mmol, 20% ketone)

Run 2 (19.0 mg, 0.0464 mmol, 15% yield, >20:1 dr; 24.9 mg, 0.0629 mmol, 21% rsm; 15.6 mg, 0.038 mmol, 13% ketone)

Run 3 (21.5 mg, 0.0525 mmol, 17% yield, >20:1 dr; 23.5 mg, 0.0594 mmol, 20% rsm; 17.2 mg, 0.042 mmol, 14% ketone)

Average overall yield: 15% (17% rsm) ± 1.5, >20:1 dr; 16% ketone

An average of 32% desired alcohol intermediate was produced in the oxidation. Lower mass balance partially resulted from the more challenging methylation procedure: approximately 80% yield in mesylation of the alcohol, and approximately 68% yield in methylation of the mesylate.

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.49-8.41 (m, 2H), 7.54 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.23 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.05 (p, *J* = 2.9 Hz, 1H), 2.67 (t, *J* = 9.9 Hz, 1H), 2.11-1.92 (m, 2H), 2.06 (s, 3H), 1.87-1.77 (m, 2H), 1.74-1.66 (m, 2H), 1.66-1.43 (m, 5H), 1.42-1.05 (m, 8H), 0.86-0.80 (m, 1H), 0.79 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.71 (q, *J* = 12.2 Hz, 1H), 0.47 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$)

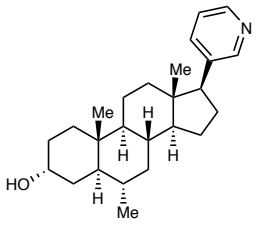
δ 170.84, 150.42, 147.50, 136.66, 135.85, 122.90, 70.05, 56.42, 54.67, 54.51, 46.52, 44.58, 41.93, 37.74, 36.15, 35.59, 33.20, 30.93, 28.93, 26.03, 25.93, 24.51, 21.73, 20.55, 20.38, 12.92, 12.51

HRMS: (ESI-TOF MS ES+)

m/z calculated for $C_{27}H_{40}NO_2$ $[M+H]^+$: 410.3059, found 410.3052.

$[\alpha]_D^{24}$ = +13.3º (c = 0.95, CH_2Cl_2)

For COSY and HSQC see Supporting Information: Spectral Data



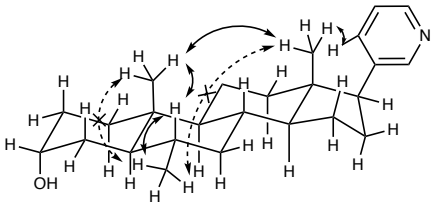
(3*R*,5*R*,6*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-6,10,13-trimethyl-17-(pyridin-3-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol [S46] Prepared by reacting **54** (7.5 mg, 0.018 mmol, 1.0 equiv.) with 1 M NaOH/MeOH (1 mL, 6 h at room temperature), the reaction mixture was partitioned between water and CH_2Cl_2, the aqueous layer was extracted with CH_2Cl_2 2x. The organic layers were combined, dried over $MgSO_4$, filtered, and condensed in vacuo to afford **S46** as a white solid (5.4 mg, 0.015 mmol, 83% yield). The stereochemistry was determined by ^{1}H NMR, COSY, and 1D NOESY methods.

^{1}H NMR: (500 MHz, $CDCl_3$)

δ 8.55-8.30 (br s, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 7.1, 4.9 Hz, 1H), 4.07 (br s, 1H), 2.67 (t, *J* = 9.8 Hz, 1H), 2.07 (dtd, *J* = 14.5, 11.1, 3.7 Hz, 1H), 2.01-1.92 (m, 1H), 1.86-1.79 (m, 1H), 1.77 (dq, *J* = 14.3, 3.0 Hz, 1H), 1.73-1.66 (m, 2H), 1.65-1.56 (m, 3H), 1.54 (dt, *J* = 11.5, 3.1 Hz, 1H), 1.51-1.42 (m, 2H), 1.40-1.25 (m, 5H), 1.24-1.10 (m, 3H), 0.88-0.82 (m, 1H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.78 (s, 3H), 0.71 (q, *J* = 12.2 Hz, 1H), 0.47 (s, 3H)

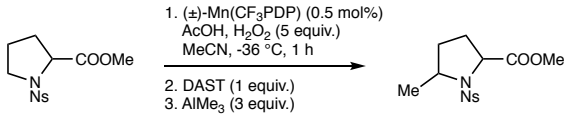
^{13}C NMR: (126 MHz, $CDCl_3$)

δ 150.47, 147.51, 135.84, 122.47, 66.54, 56.42, 54.66, 54.64, 45.64, 44.58, 42.01, 37.76, 36.46, 35.63, 32.49, 31.81, 31.00, 28.81, 26.04, 24.52, 20.54, 20.40, 12.93, 12.35

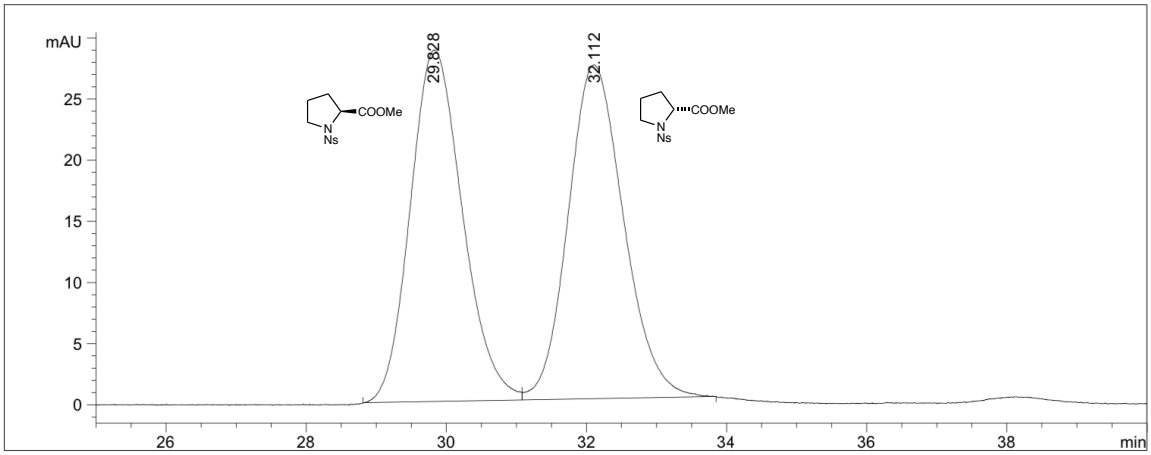


For COSY and NOESY see Supporting Information: Spectral Data

VII. HPLC traces for the determination of product stereoretention



HPLC (Chiralcel OJ-H, 1.0 mL/min, 30 °C, 98:2 Hex:iPrOH) trace for the racemic starting material:

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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Totals :                  2992.62781   56.03881
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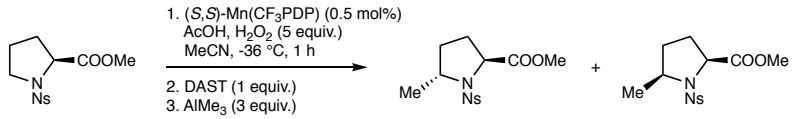
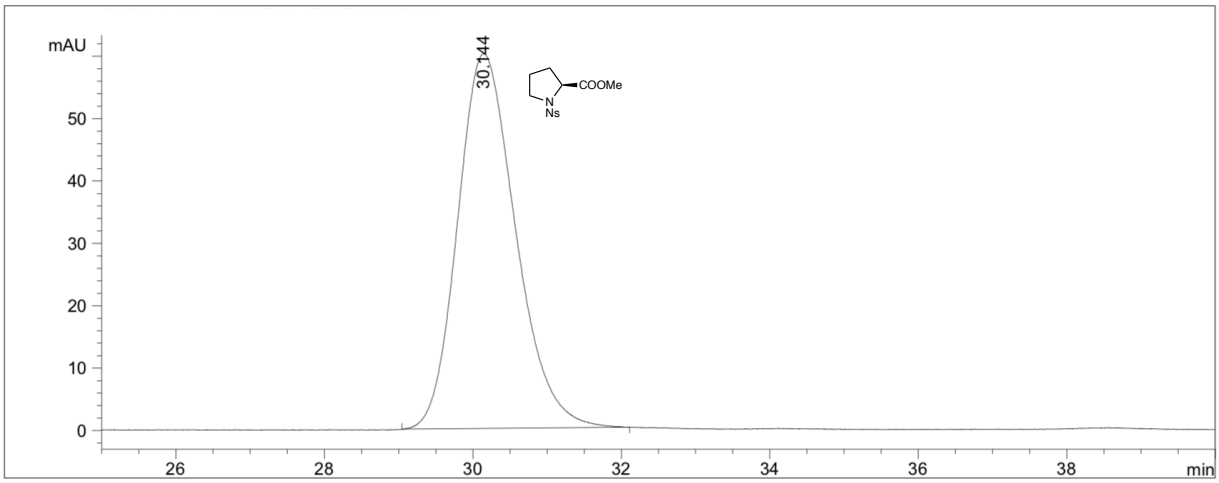


HPLC (Chiralcel OJ-H, 1.0 mL/min, 30 °C, 98:2 Hex:iPrOH) trace for chiral starting material **S11**:

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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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Totals :                  3258.70850   60.07316
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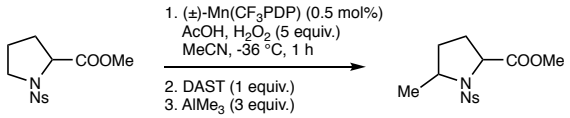
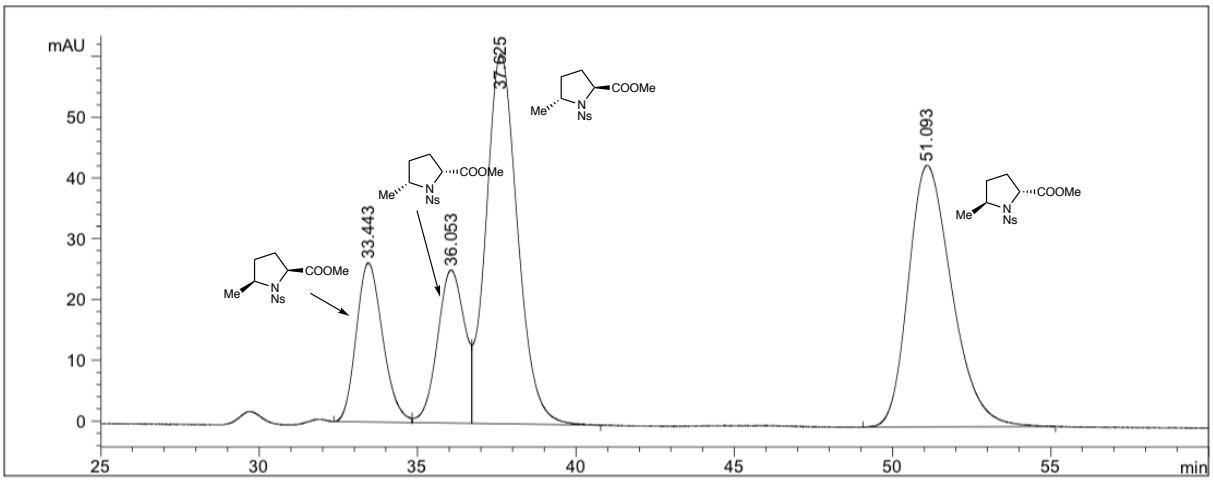
>99% ee according to the HPLC trace integration.



HPLC (Chiralcel OJ-H, 1.0 mL/min, 30 °C, 98:2 Hex:iPrOH) trace for the racemic methylation product:

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Sorted By             :      Signal
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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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   2  36.053 VV    0.8652 1505.18762   25.18344  13.2473
   3  37.625 VB    1.0371 4233.38037   60.82311  37.2584
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Totals :                 1.13622e4   155.19114
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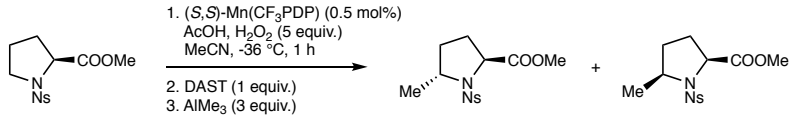
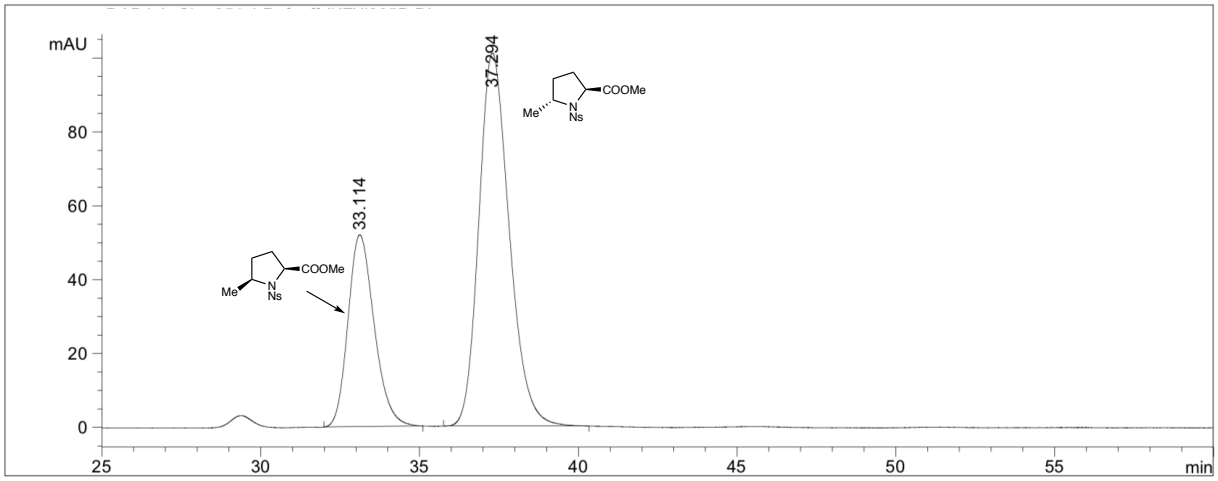


HPLC (Chiralcel OJ-H, 1.0 mL/min, 30 °C, 98:2 Hex:iPrOH) trace for chiral product **12**:

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

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Totals :                  9709.02222  152.97834
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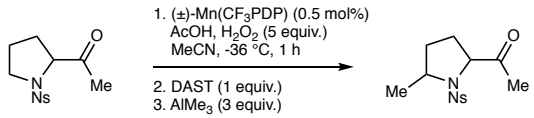
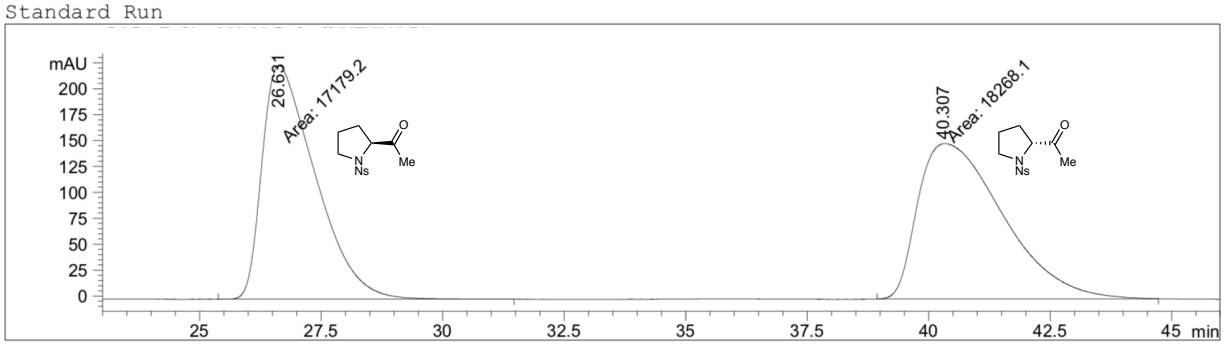
>99% ee according to the HPLC trace integration, 100% es.



HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the racemic starting material:

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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

Peak RetTime Type  Width     Area      Height     Area
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Totals :                  3.54473e4   375.76149
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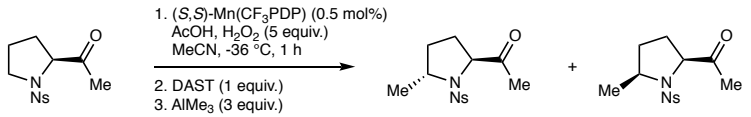
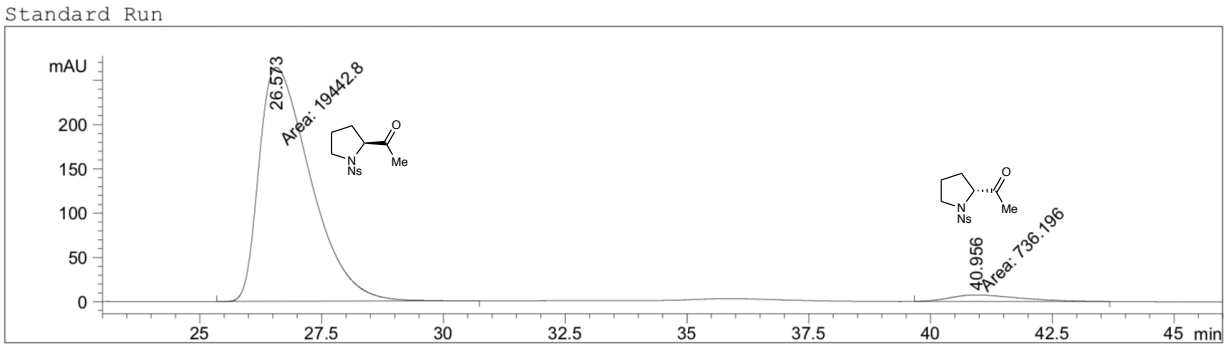


HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the chiral starting material **S12**:

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Sorted By             :      Signal
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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

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Totals :                  2.01790e4   271.60394
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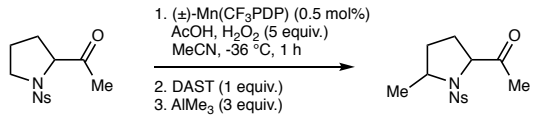
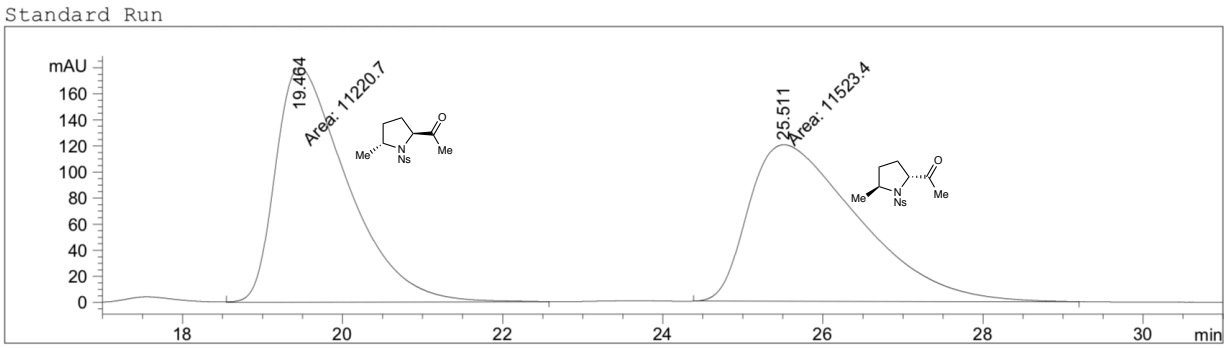
93% ee according to the HPLC trace integration.



HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the racemic major product:




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.464 MM    1.0391 1.12207e4   179.97972  49.3347
   2  25.511 MM    1.5991 1.15234e4   120.10565  50.6653

Totals :                 2.27441e4   300.08537
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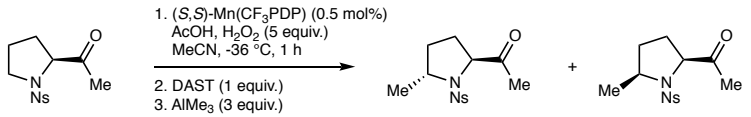
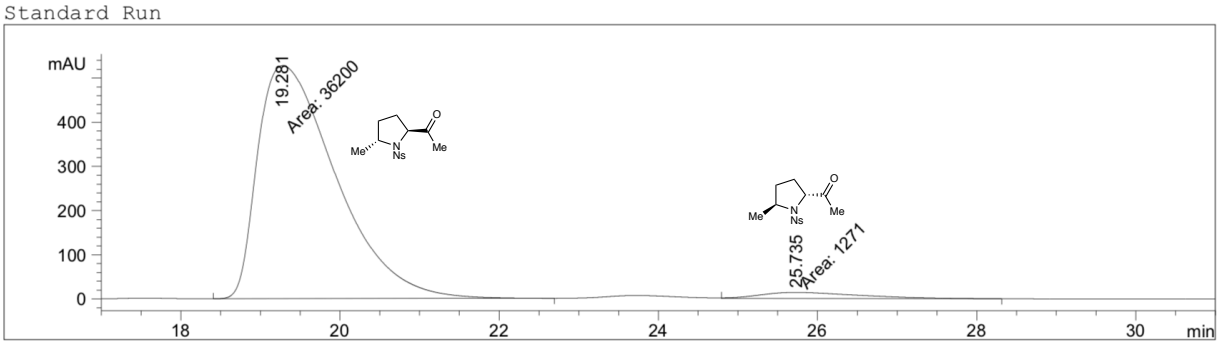


HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the chiral major product **13**:

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.281 MM    1.1428 3.62000e4   527.94159  96.6080
   2  25.735 MM    1.4844 1271.00012   14.27045   3.3920

Totals :                  3.74710e4   542.21204
```
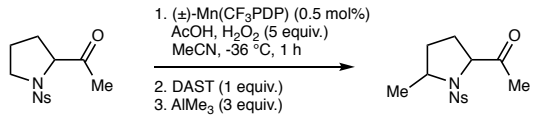
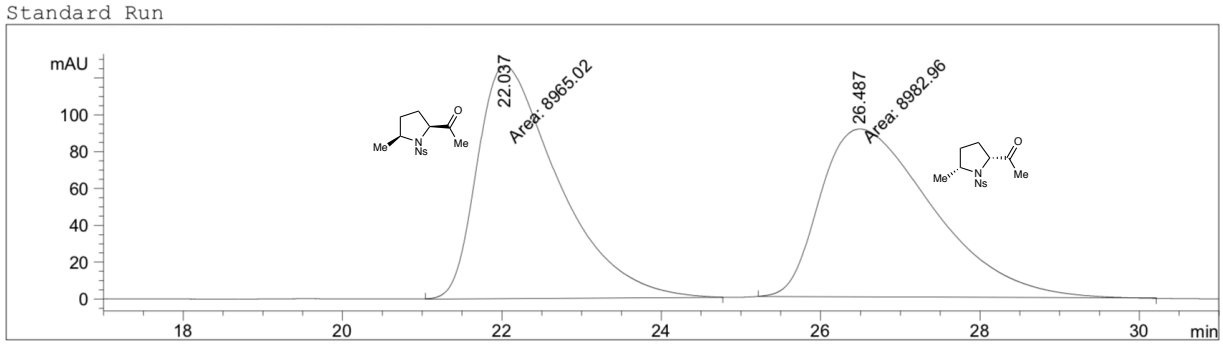

93% ee according to the HPLC trace integration, 100% es.



HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the racemic minor product:




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.037 MM    1.1798 8965.02148  126.64558  49.9500
   2  26.487 MM    1.6407 8982.95508   91.24899  50.0500

Totals :                 1.79480e4   217.89457
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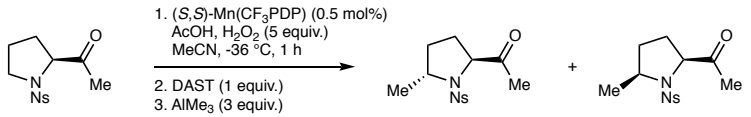
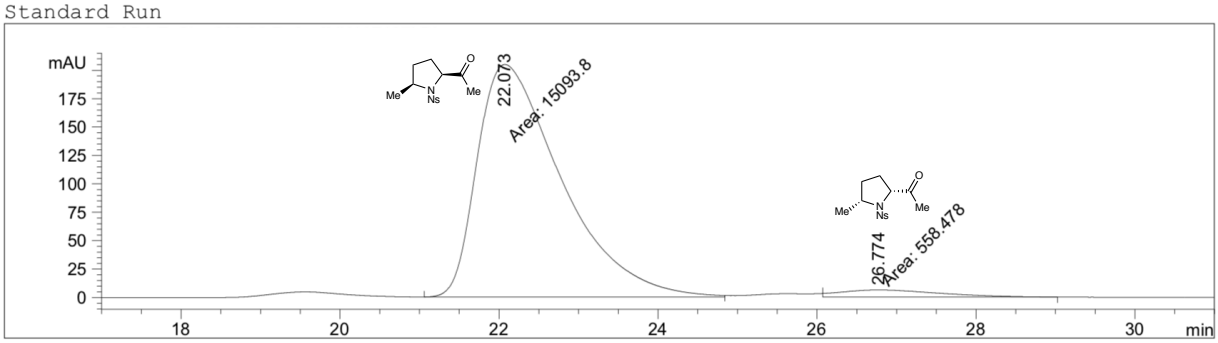


HPLC trace (AD-RH Reverse Phase Chiral, 1.0 mL/min, 30 °C, 35:65 MeCN:H_2O) for the chiral minor product **S28**:

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 E, Sig=280,20 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.073 MM    1.2289 1.50938e4   204.70573  96.4320
   2  26.774 MM    1.4667  558.47784    6.34629   3.5680

Totals :                  1.56523e4   211.05202
```

93% ee according to the HPLC trace integration, 100% es.

VIII. References

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6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
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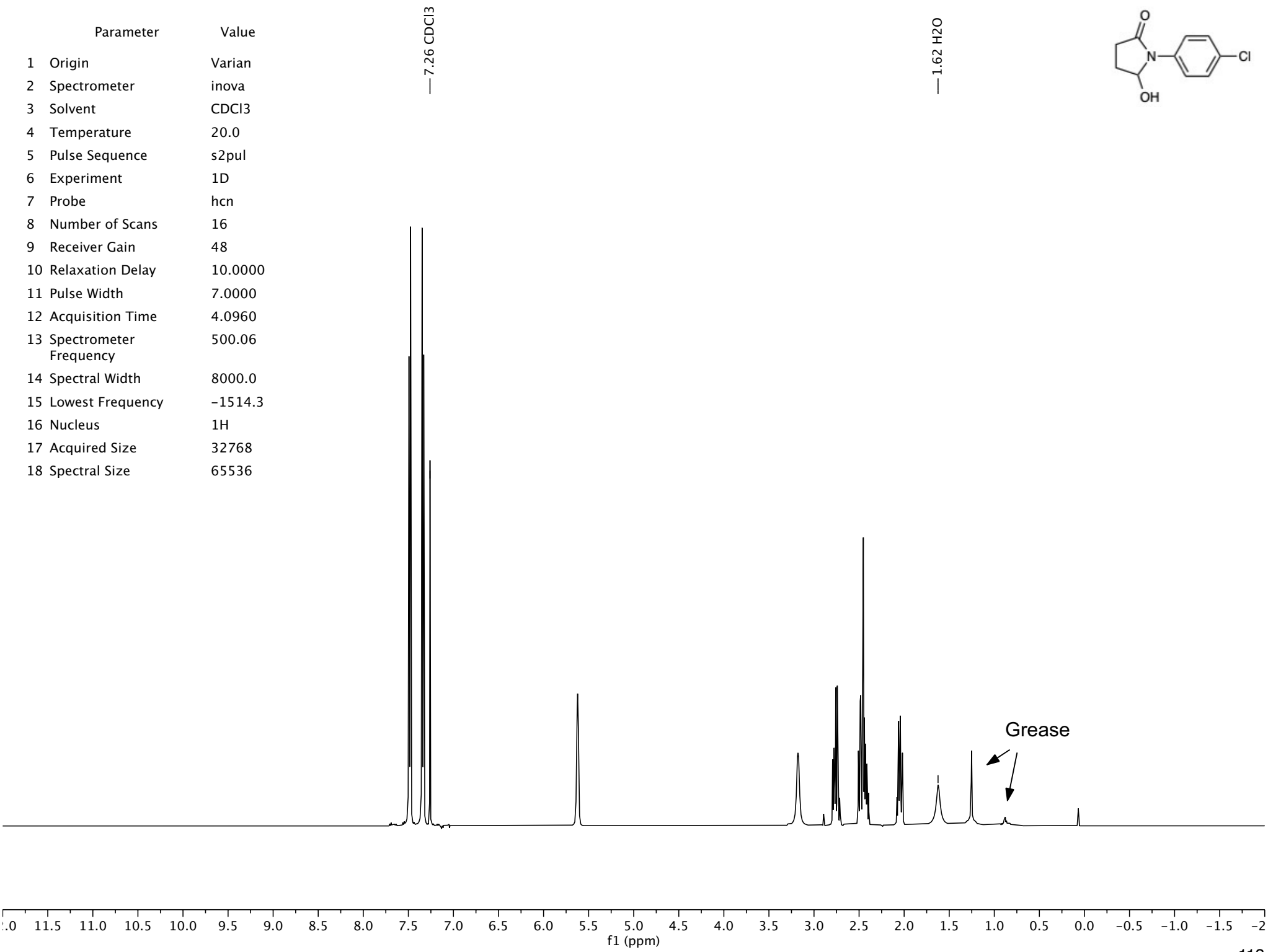
15	Lowest Frequency	-1514.3
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
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2	Spectrometer	spect
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4	Temperature	296.1
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7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
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17	Acquired Size	32768
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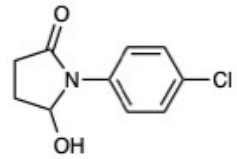

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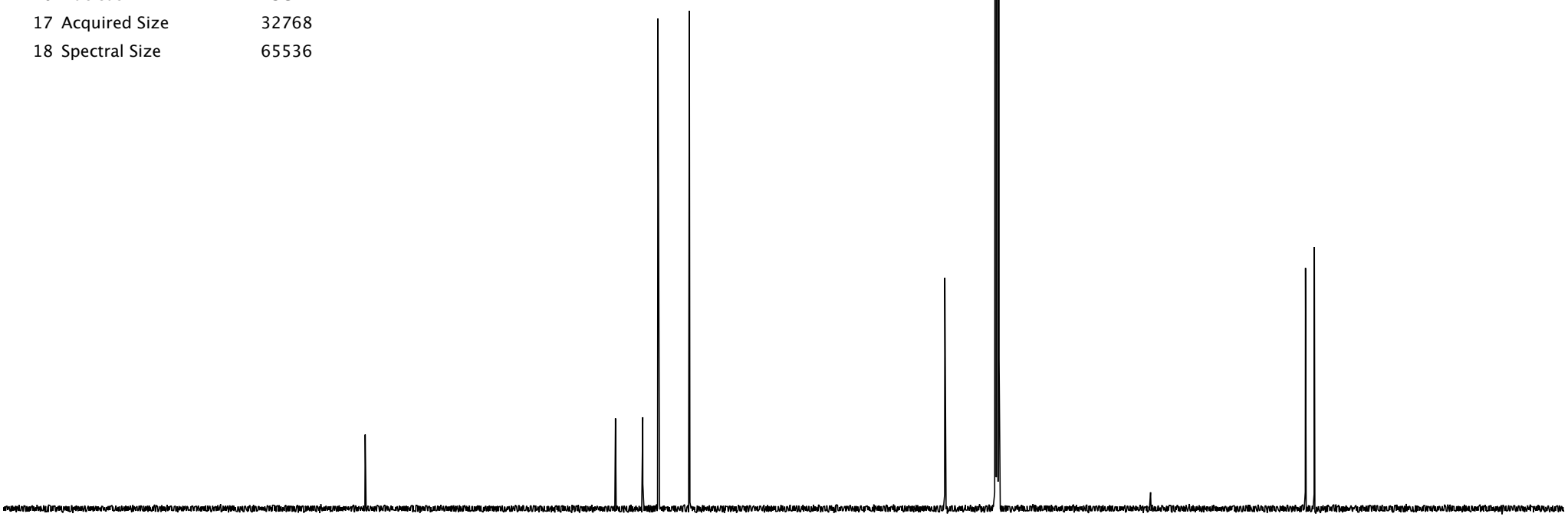

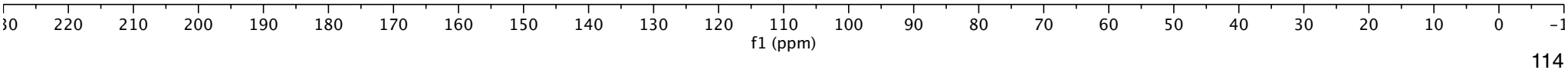

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7	Probe	quadbp
8	Number of Scans	16
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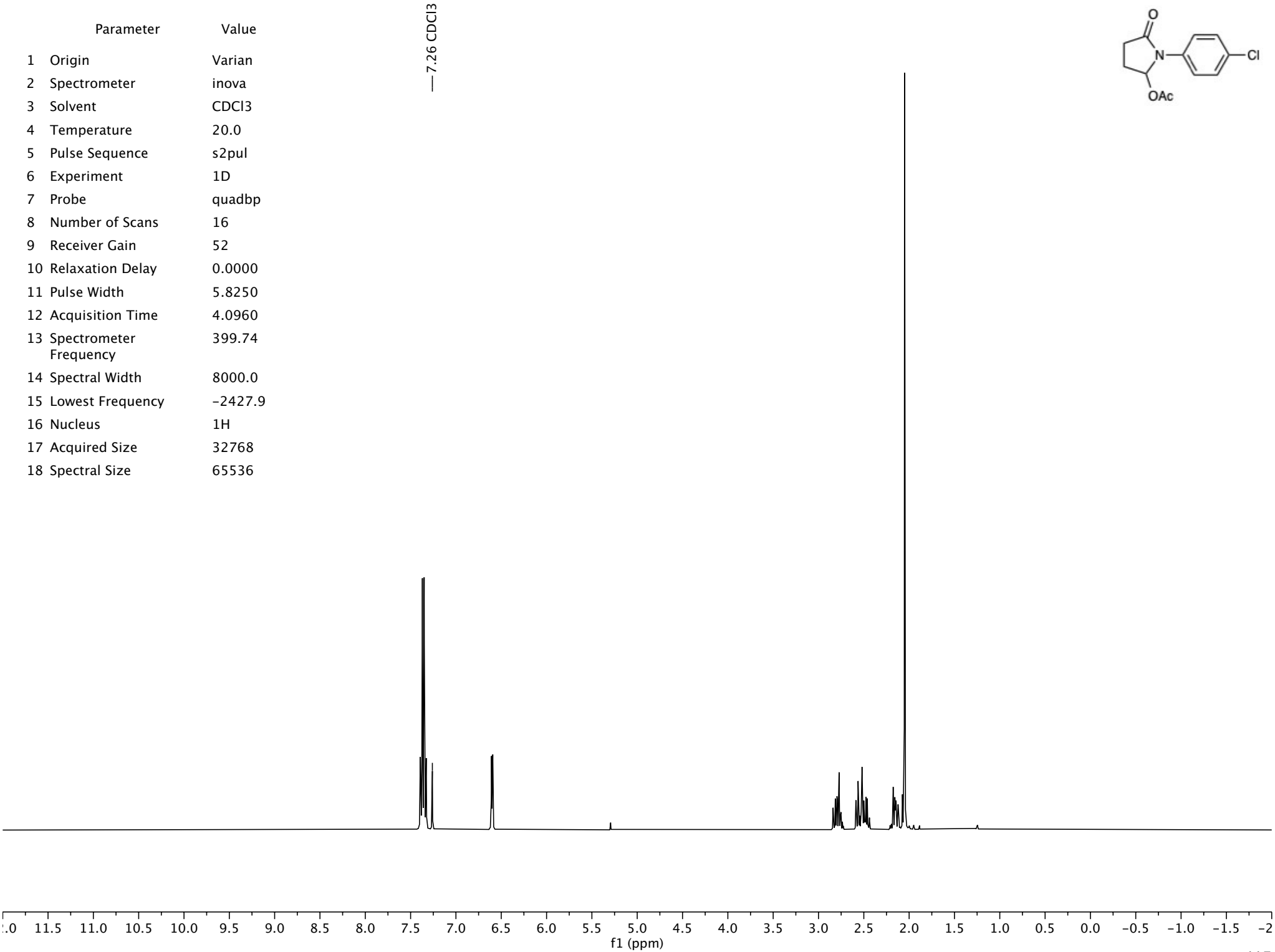

	Parameter	Value
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2	Spectrometer	spect
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4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	128
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10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
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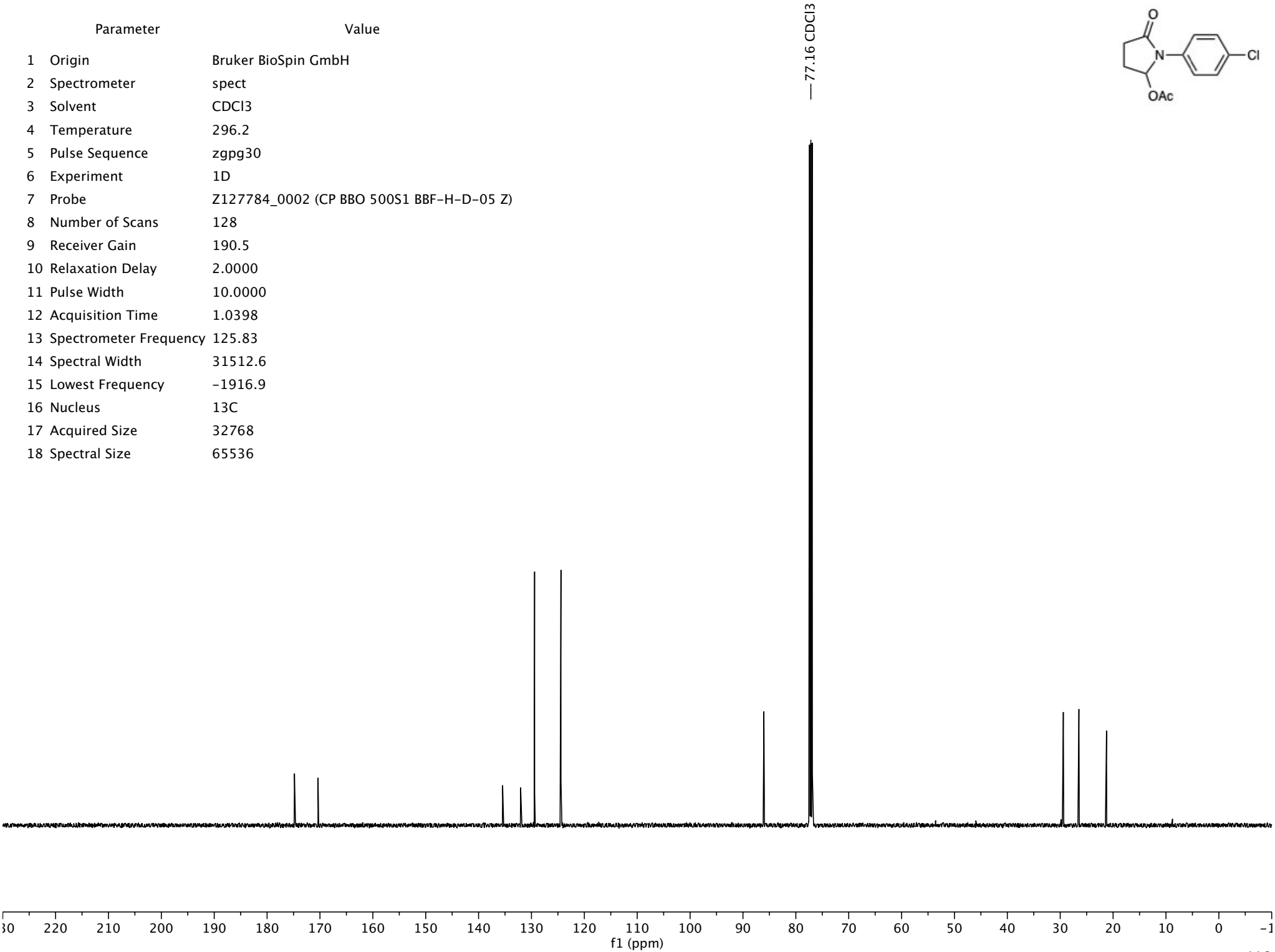
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
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3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUADG
8	Number of Scans	16
9	Receiver Gain	44
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11	Pulse Width	12.1250
12	Acquisition Time	4.0960
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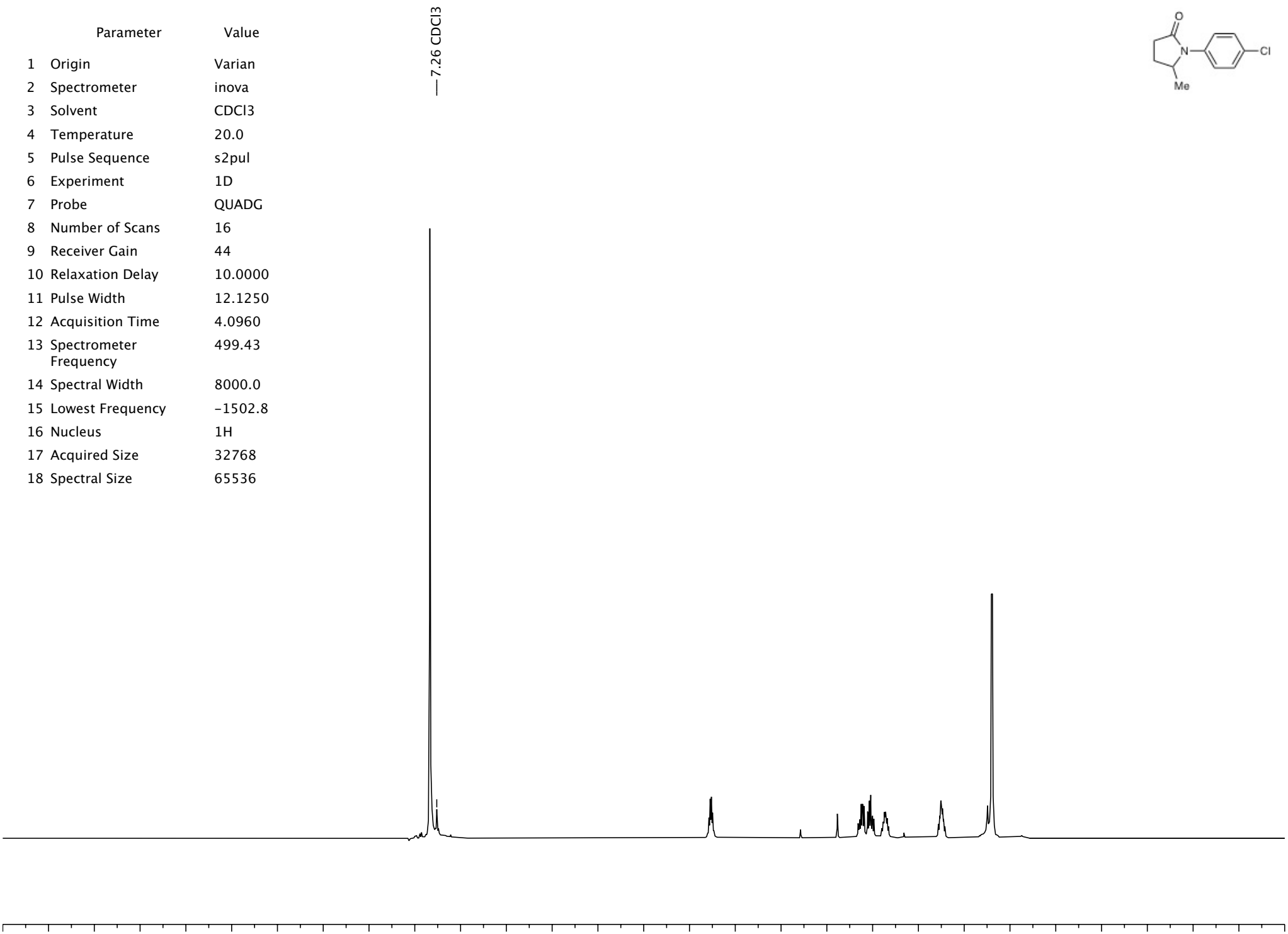

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2	Spectrometer	inova
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7	Probe	QUADG
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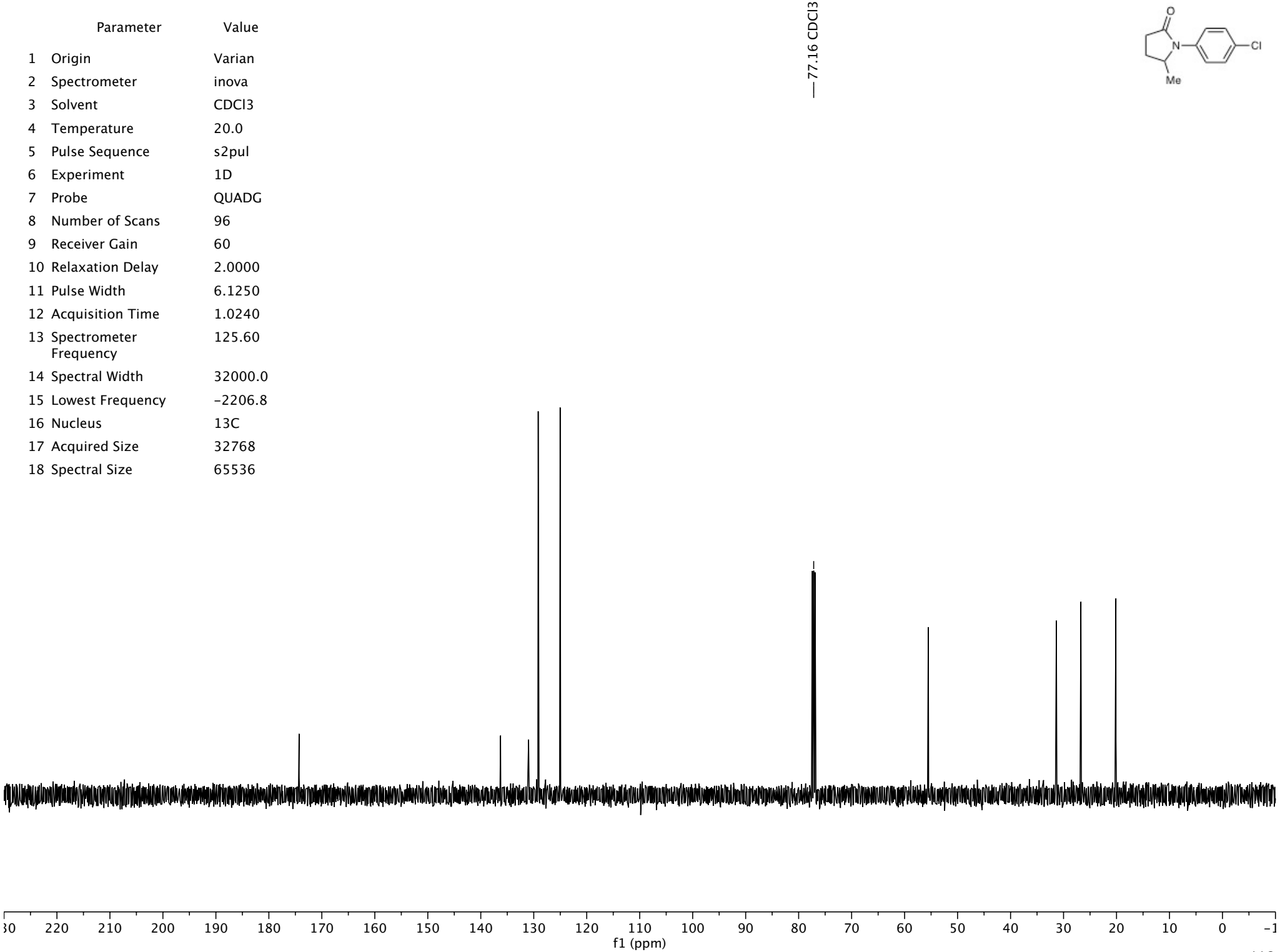

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2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
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11	Pulse Width	7.0000
12	Acquisition Time	4.0960
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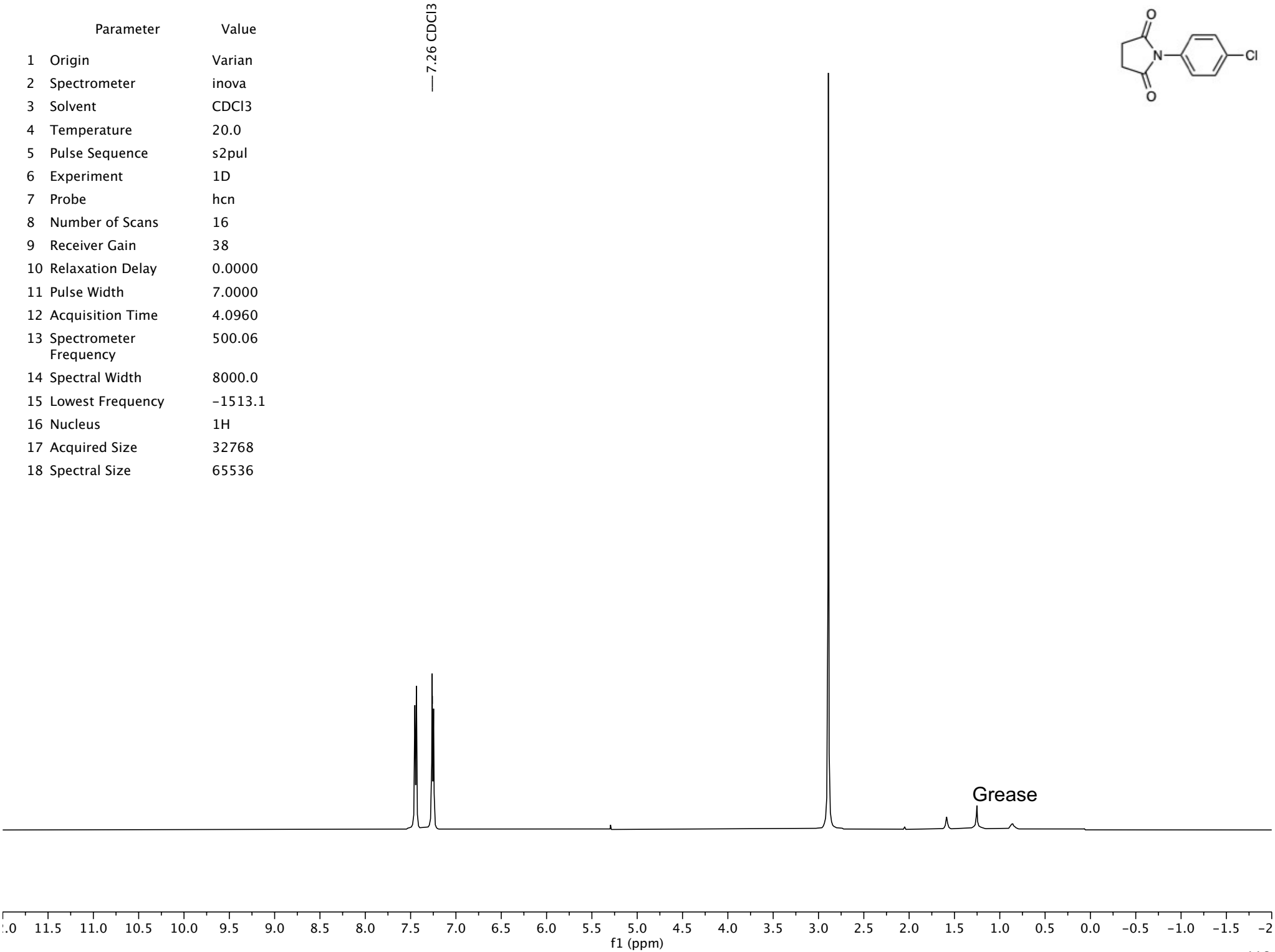
18	Spectral Size	65536



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7	Probe	hcn
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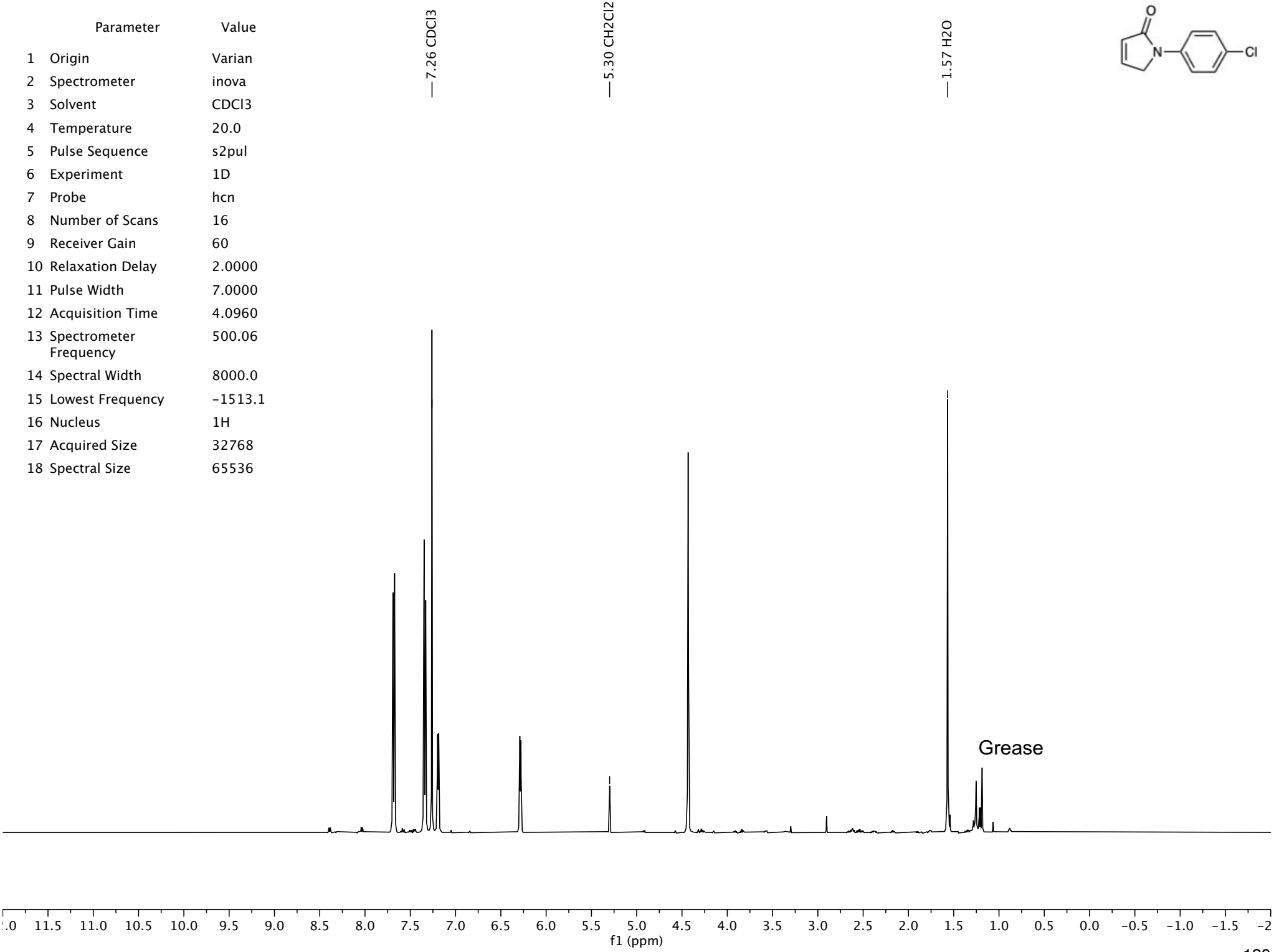

	Parameter	Value
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2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
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16	Nucleus	13C
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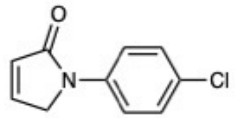
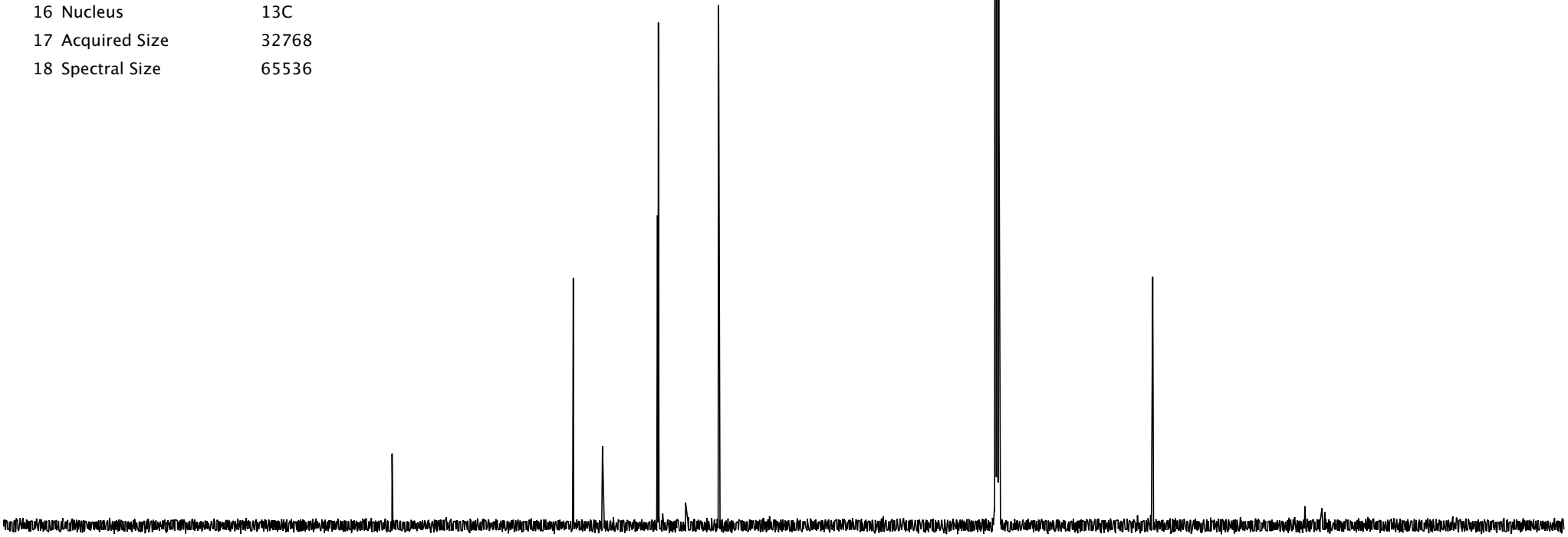
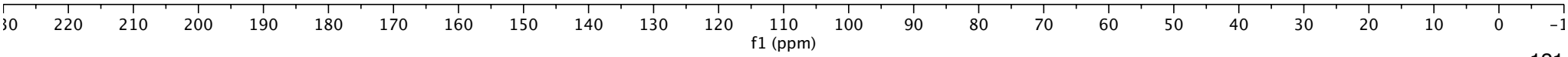


77.16 CDCl3





	Parameter	Value
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4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	44
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
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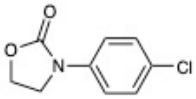
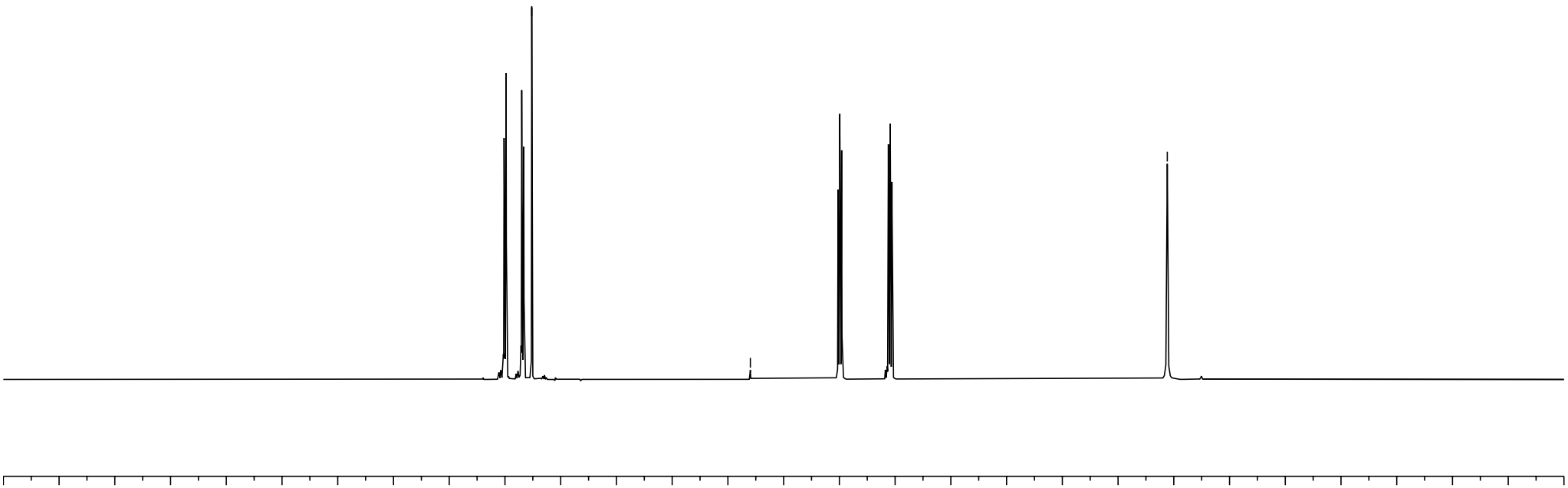
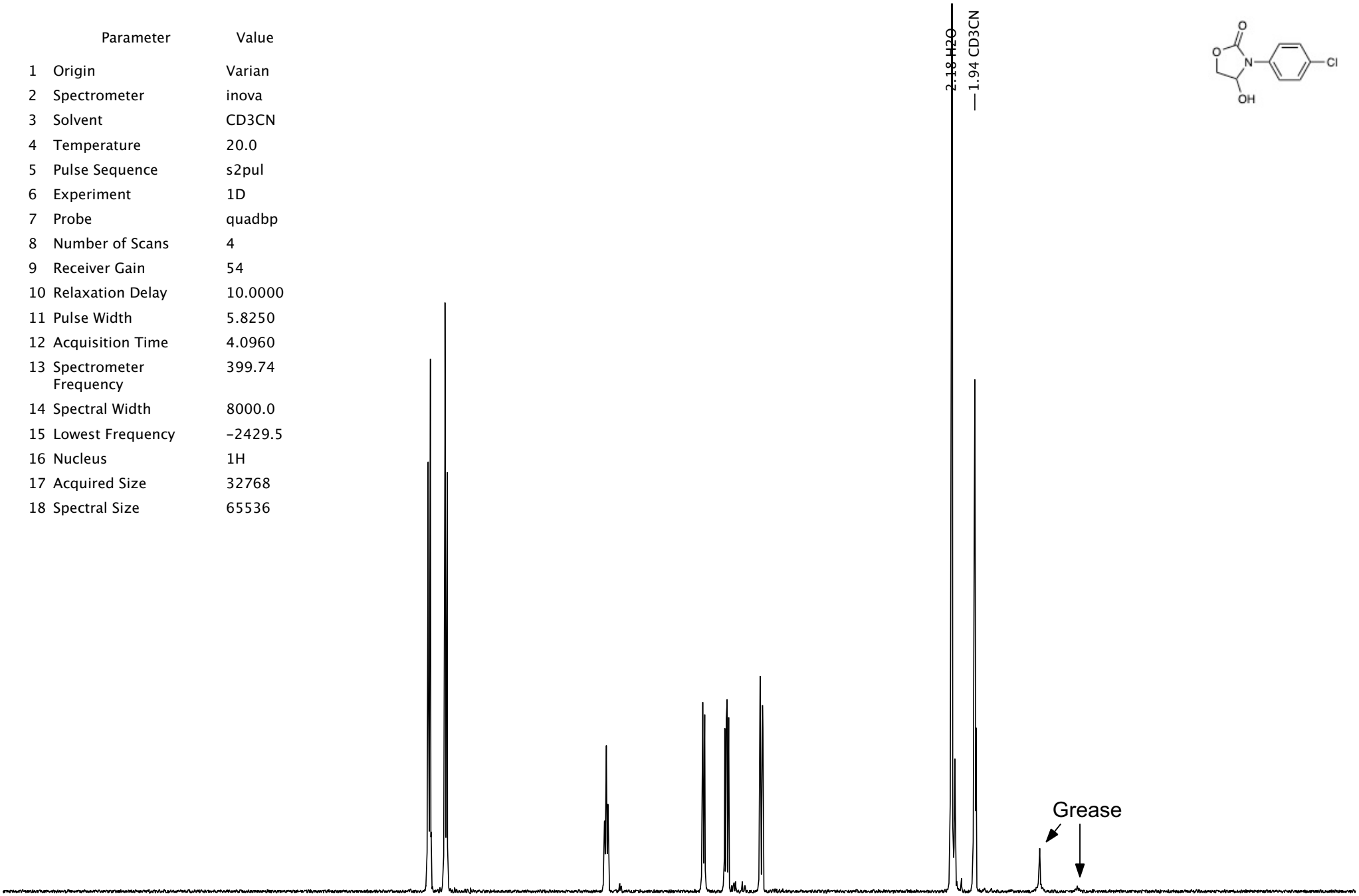
18	Spectral Size	65536

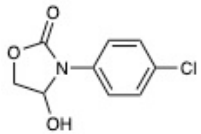


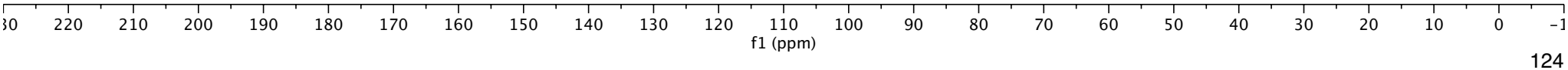


	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CD3CN
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	4
9	Receiver Gain	54
10	Relaxation Delay	10.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2429.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

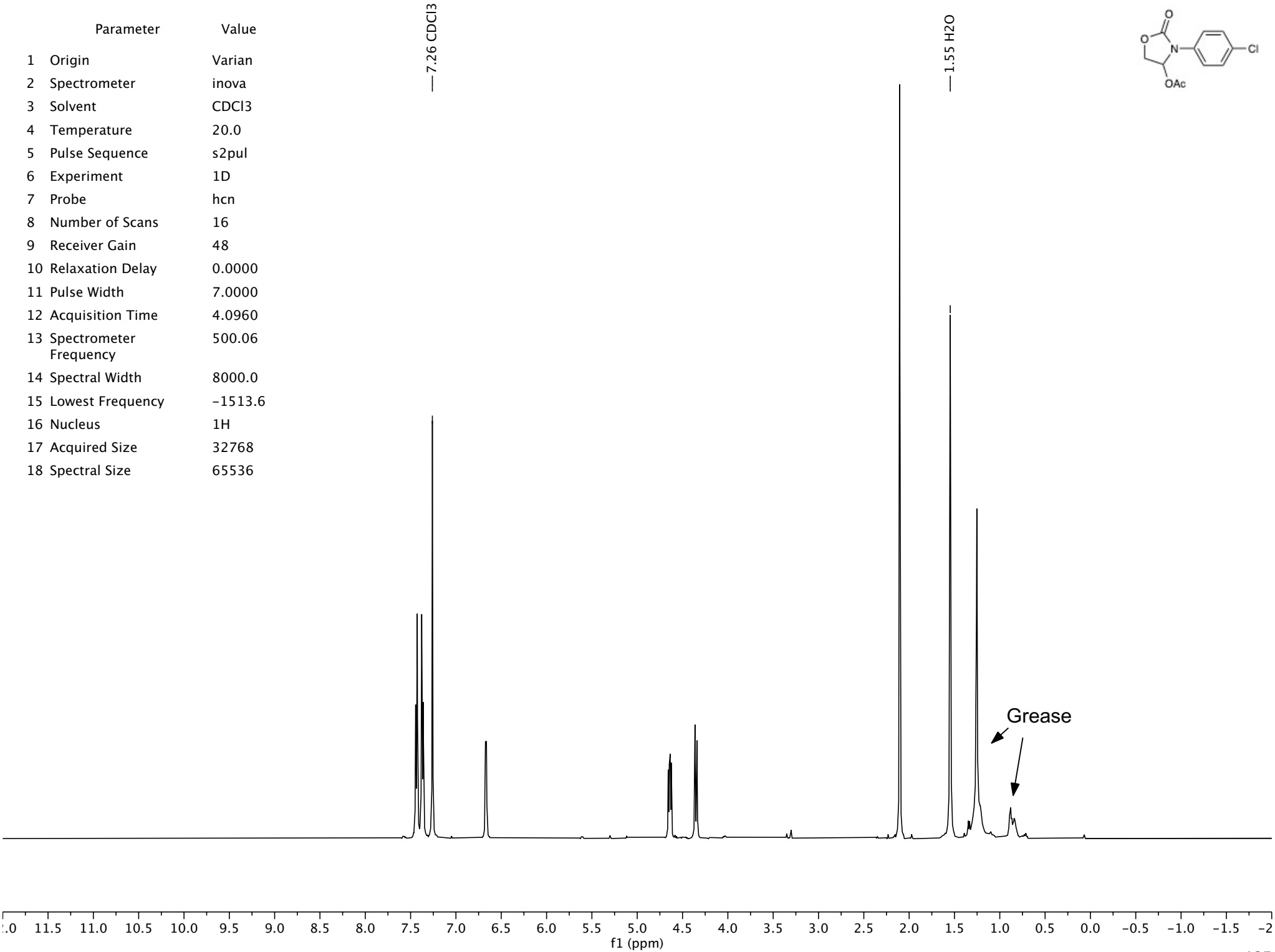


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CD3CN
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1798.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

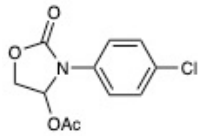




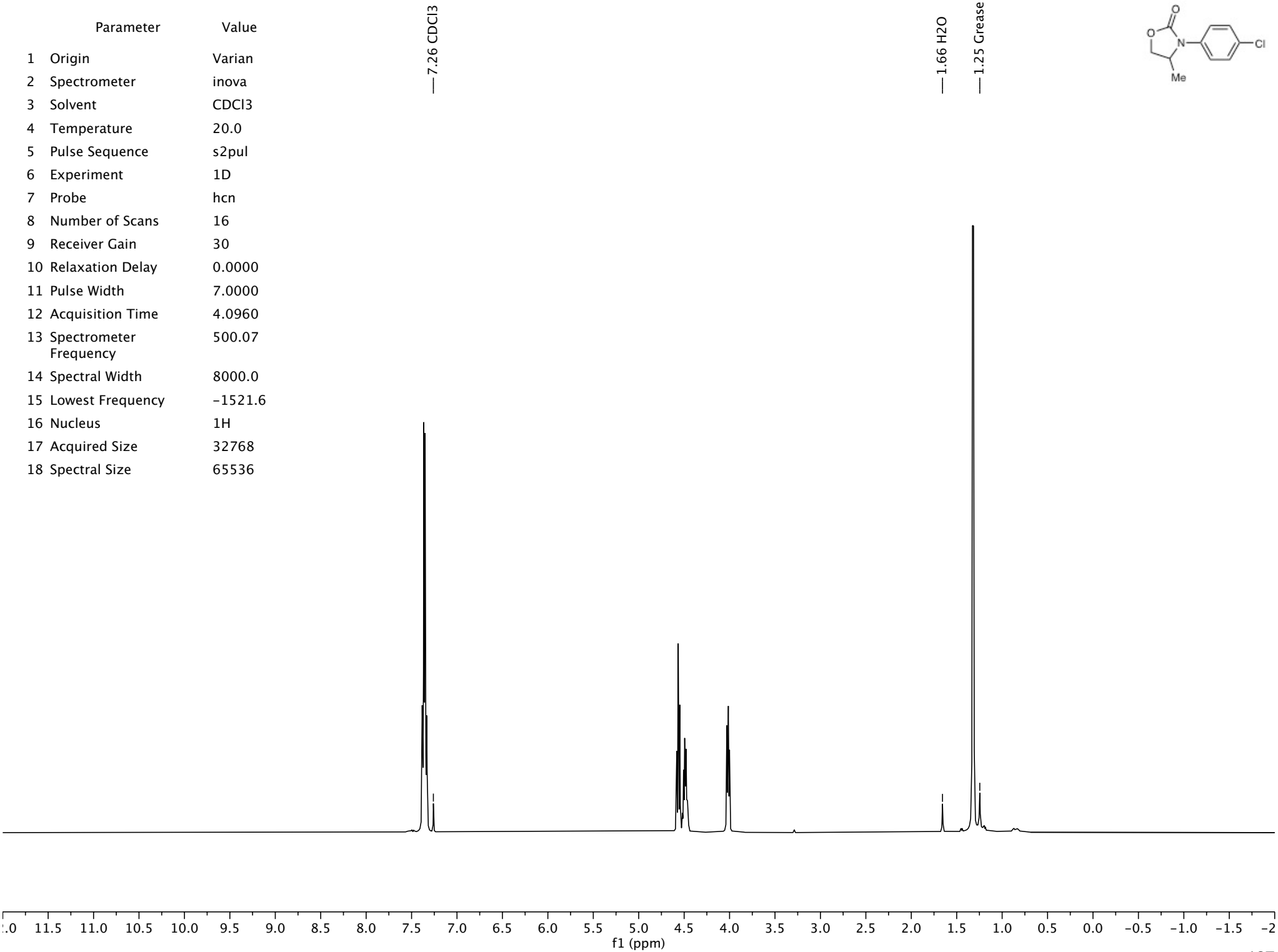
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.2
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

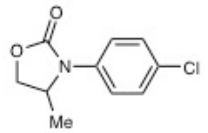


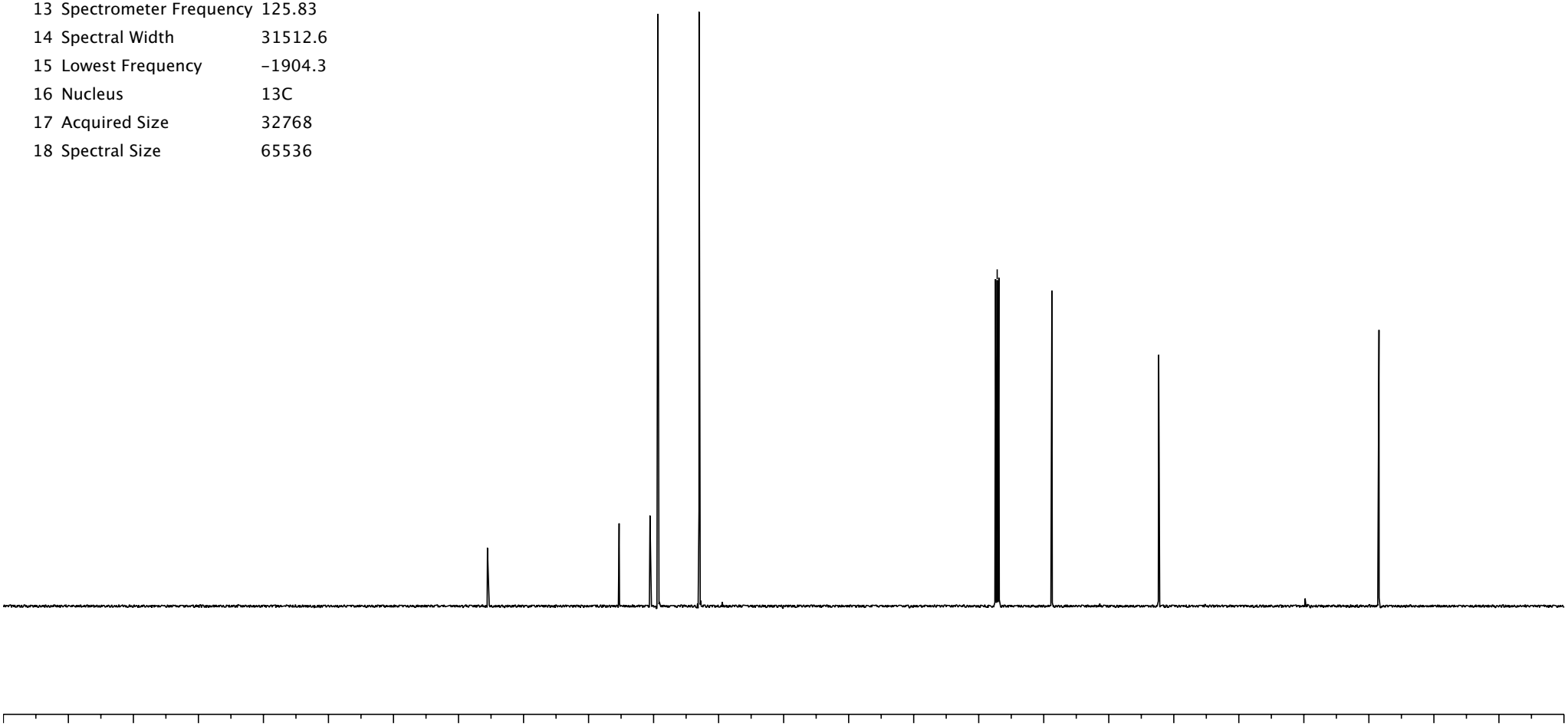
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	30
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	128
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1904.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

77.16 CDCl3

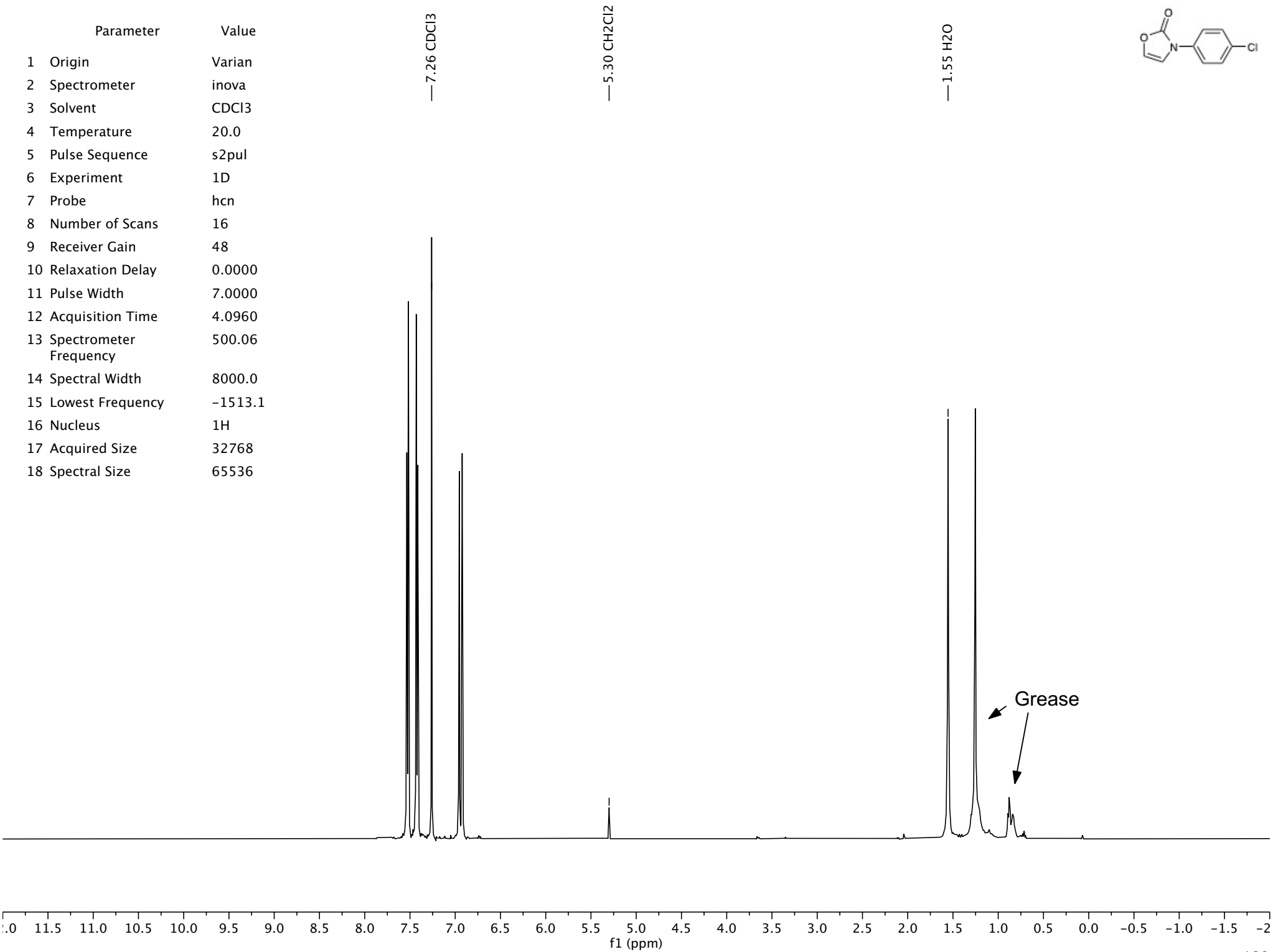




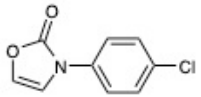
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

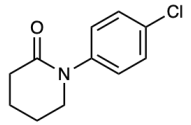


77.16 CDCl3

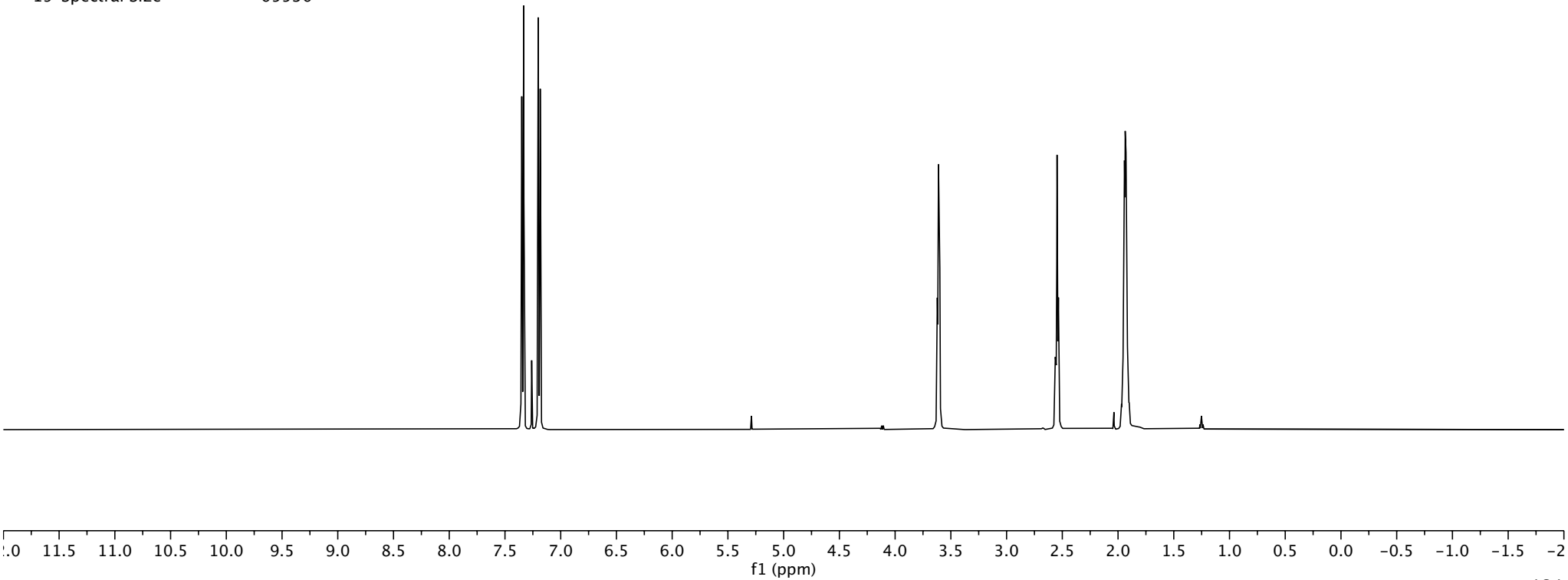
Grease

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

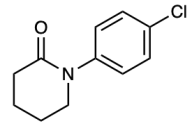
f1 (ppm)

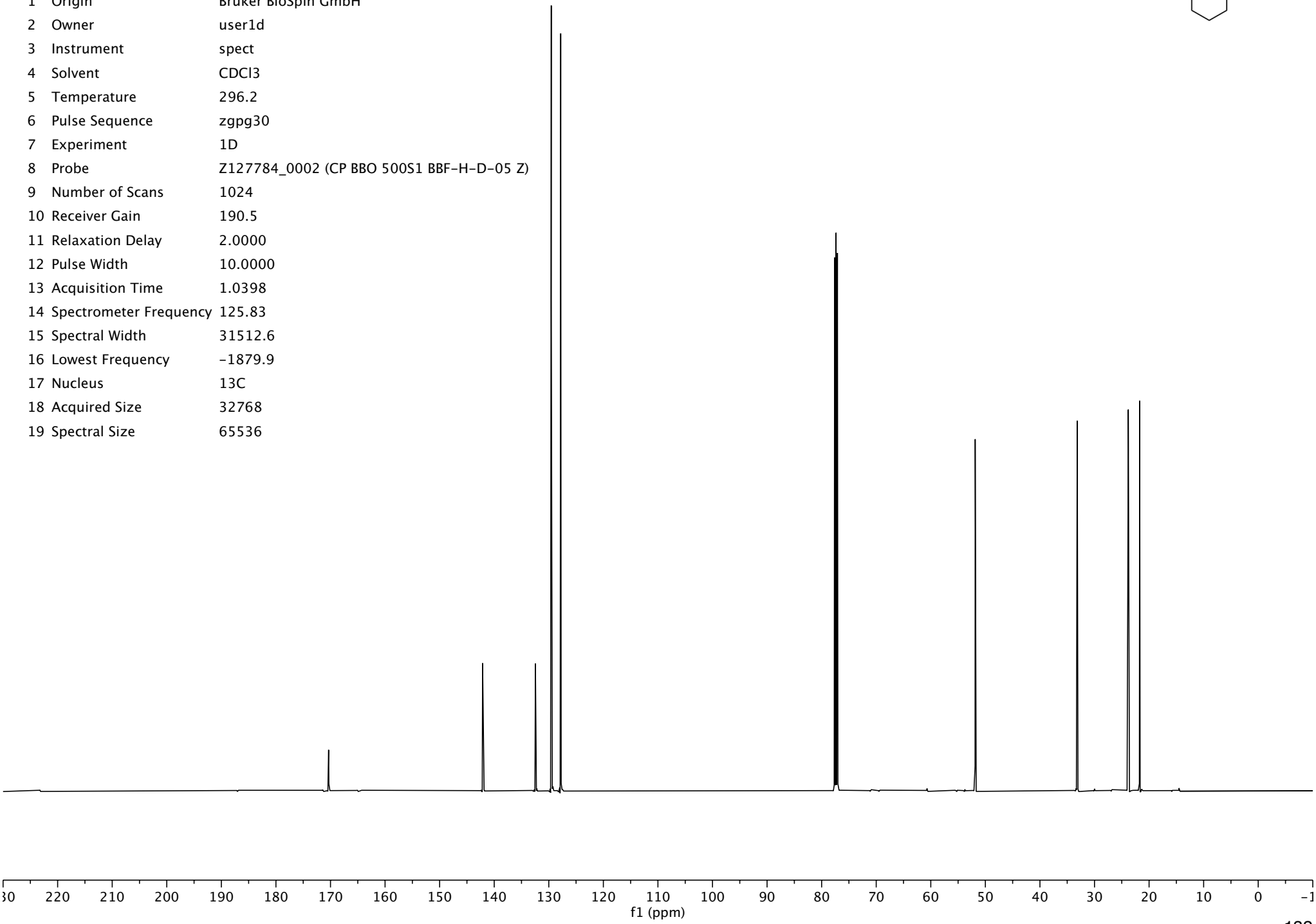


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	61.8
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

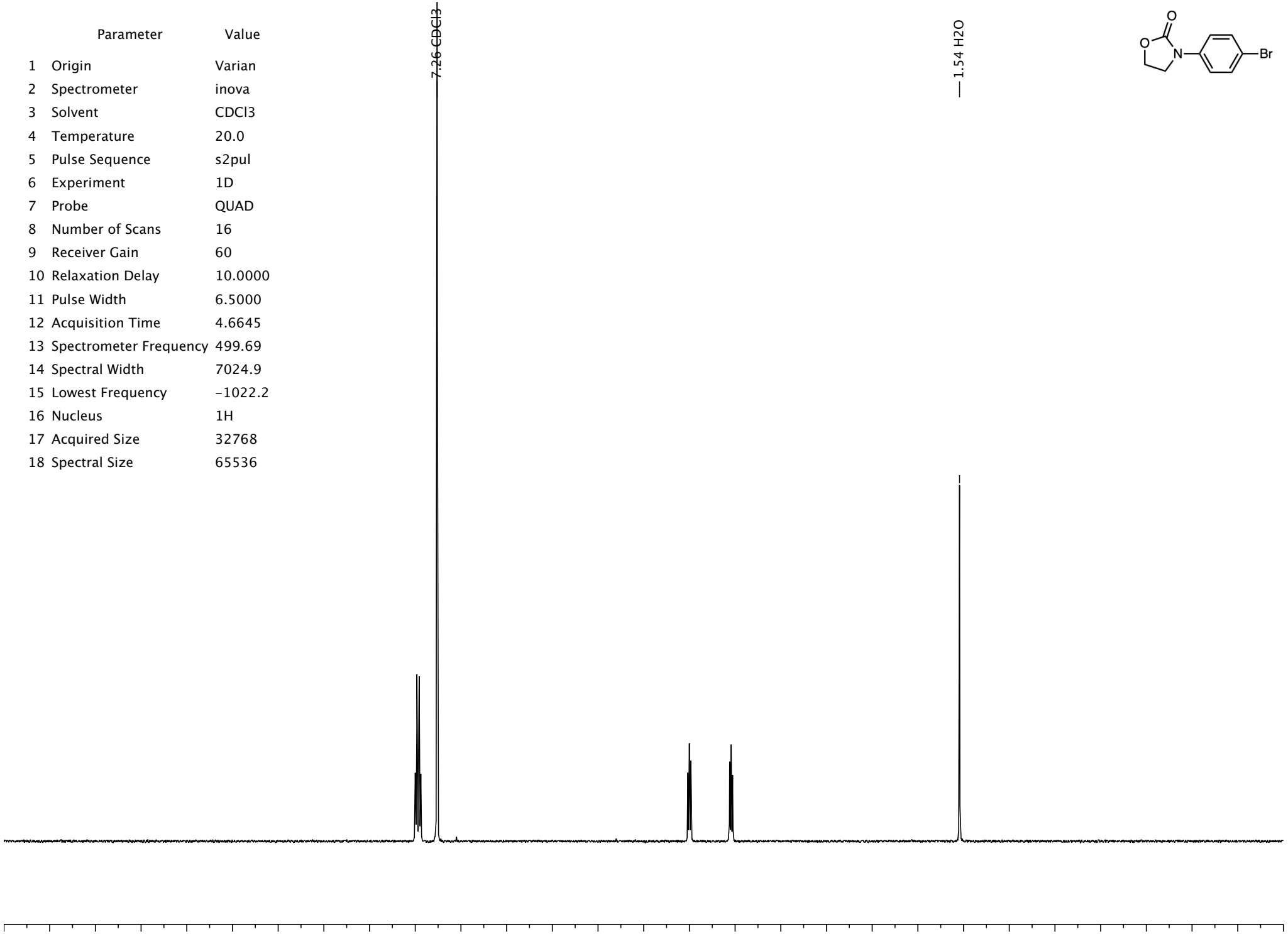


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1879.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

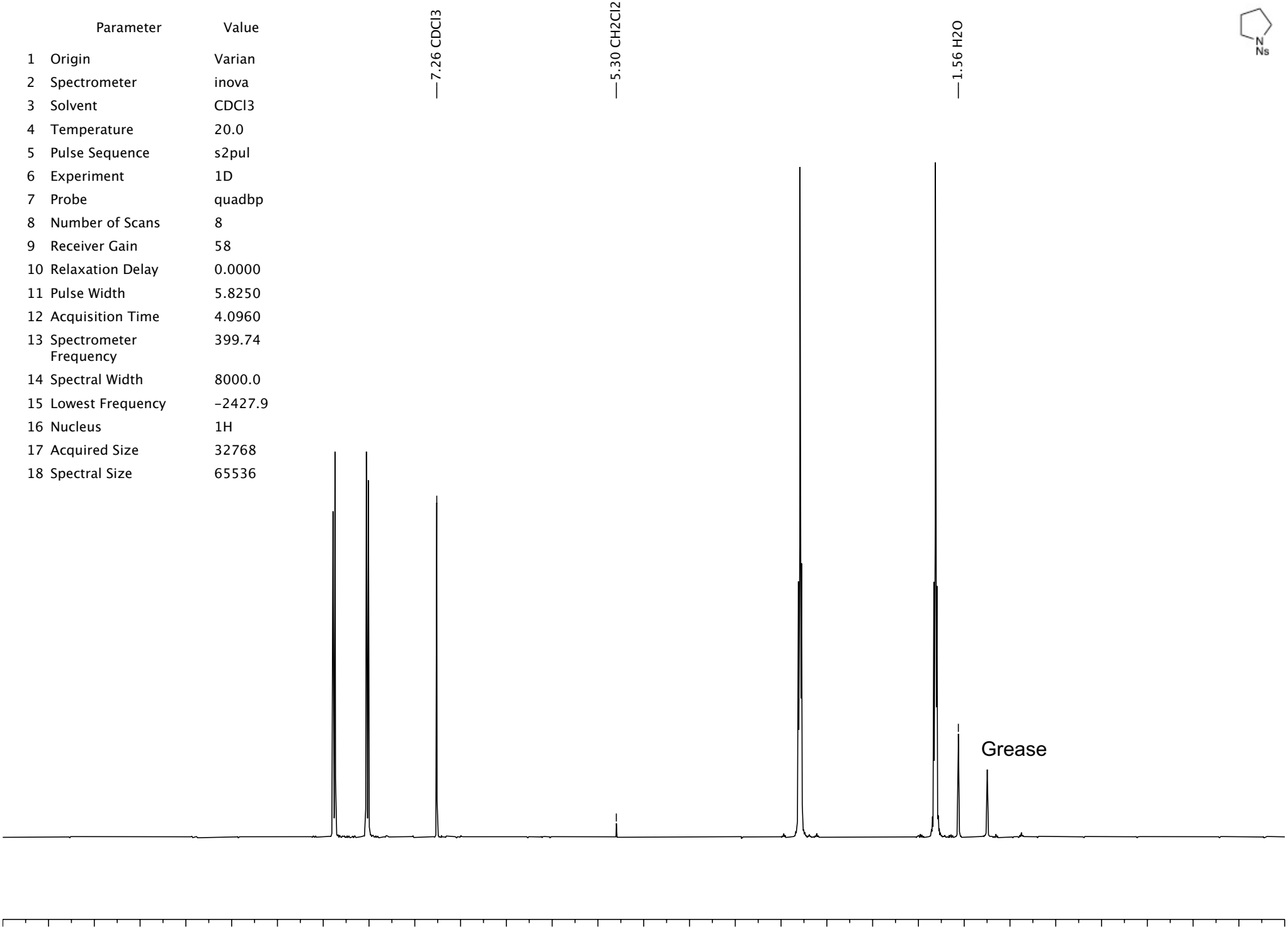




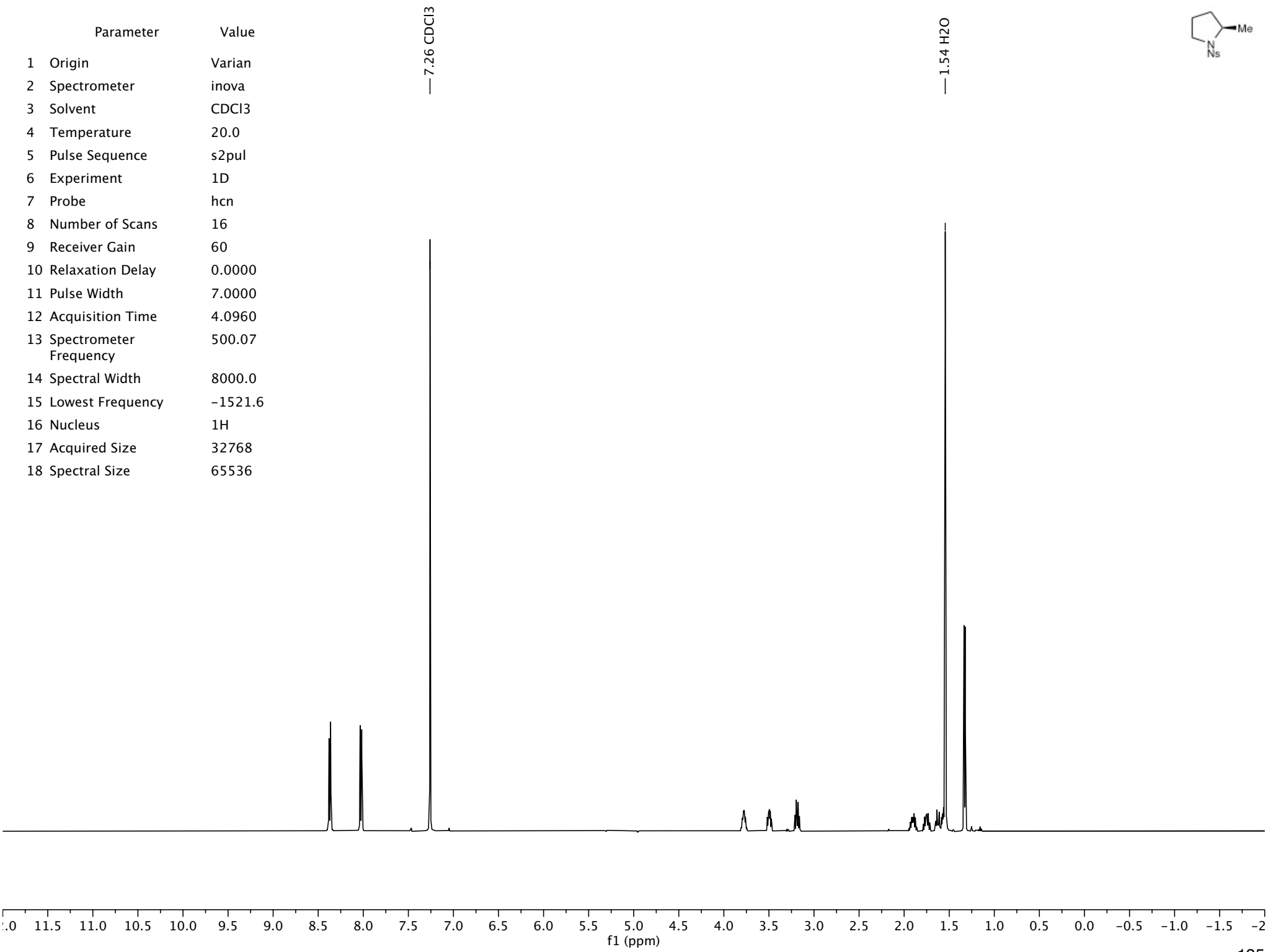
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1022.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



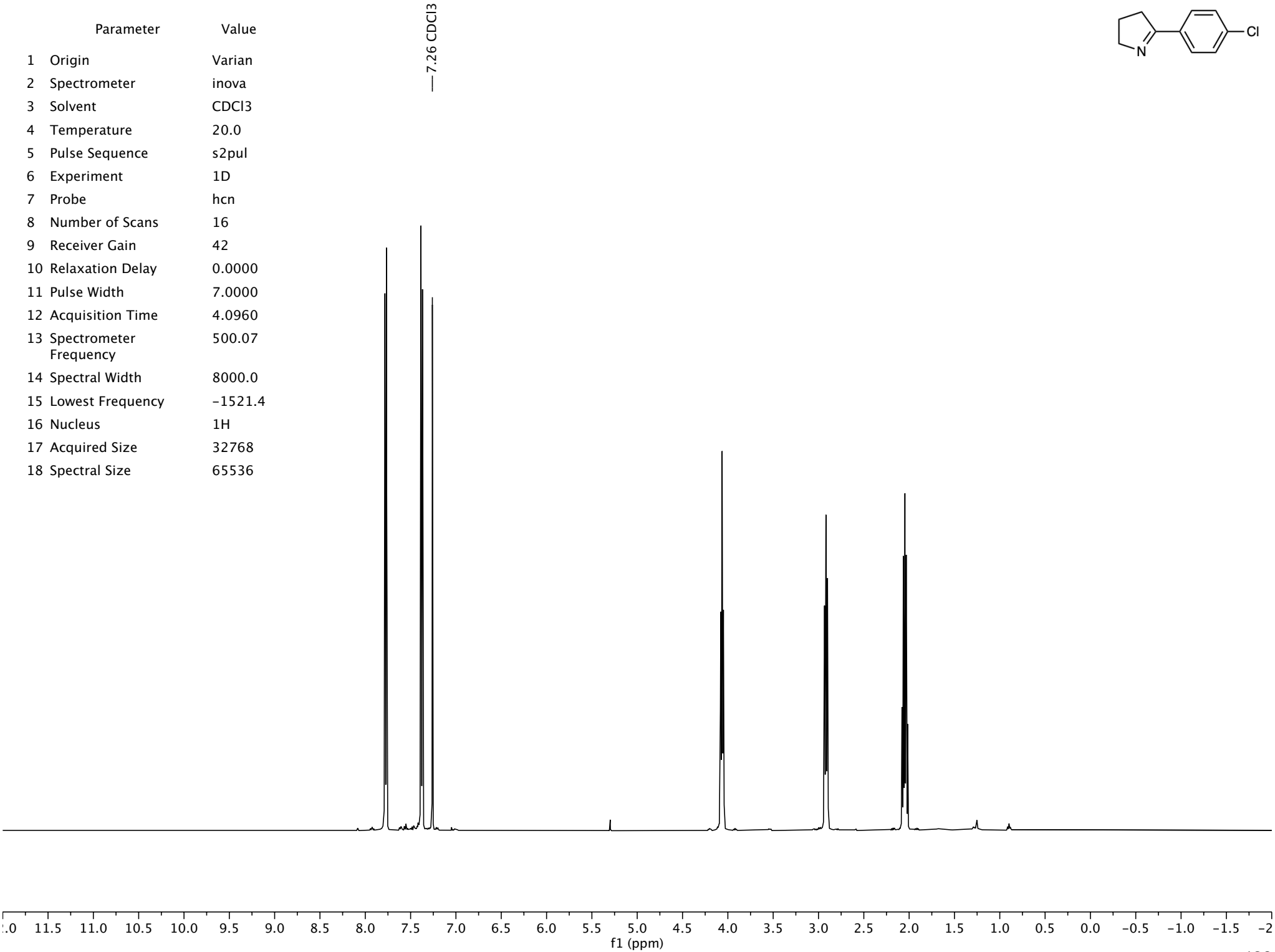
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	8
9	Receiver Gain	58
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



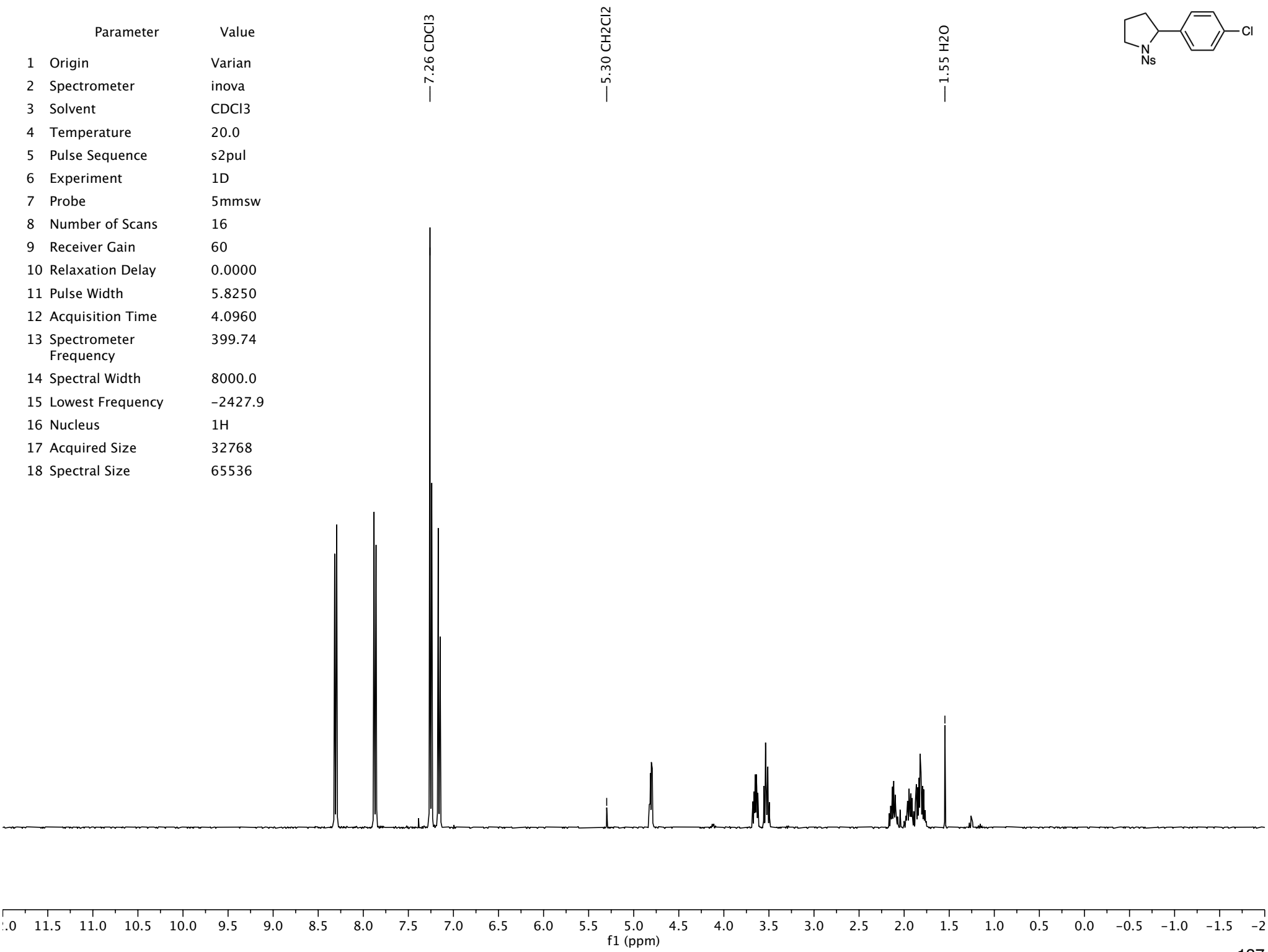
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



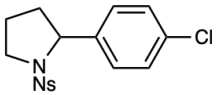
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	5mmsw
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

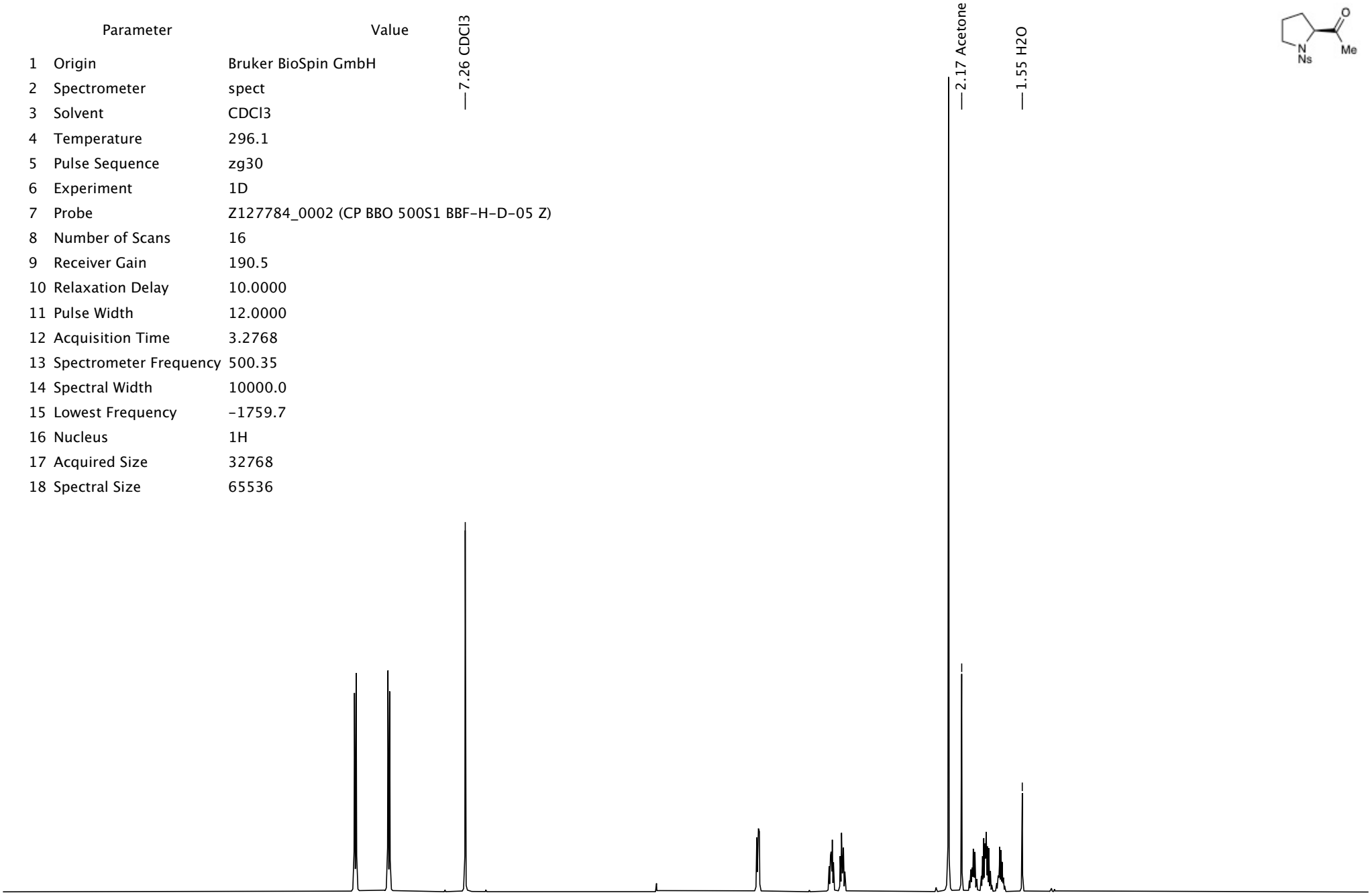


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

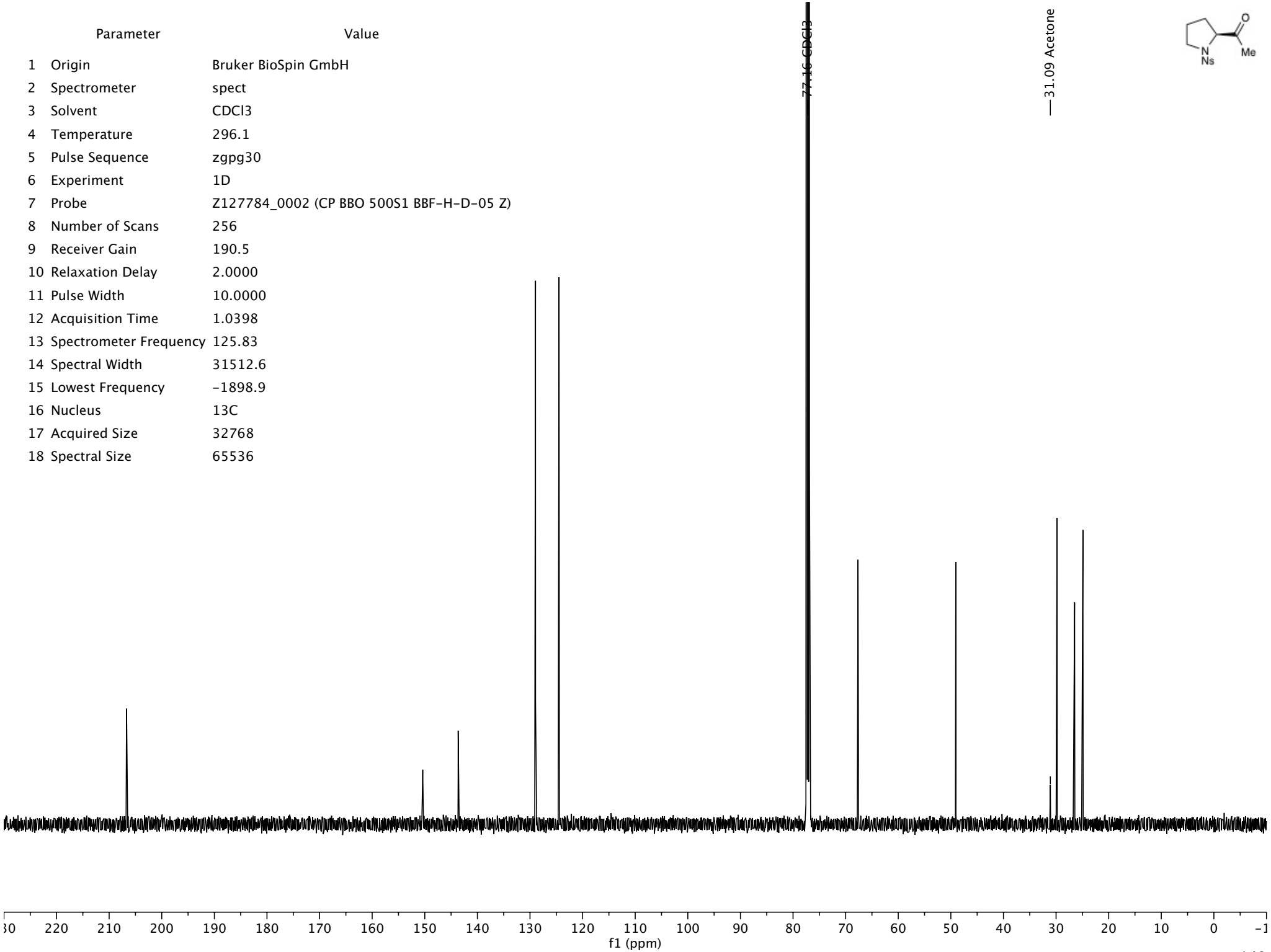


77.16 CDCl3

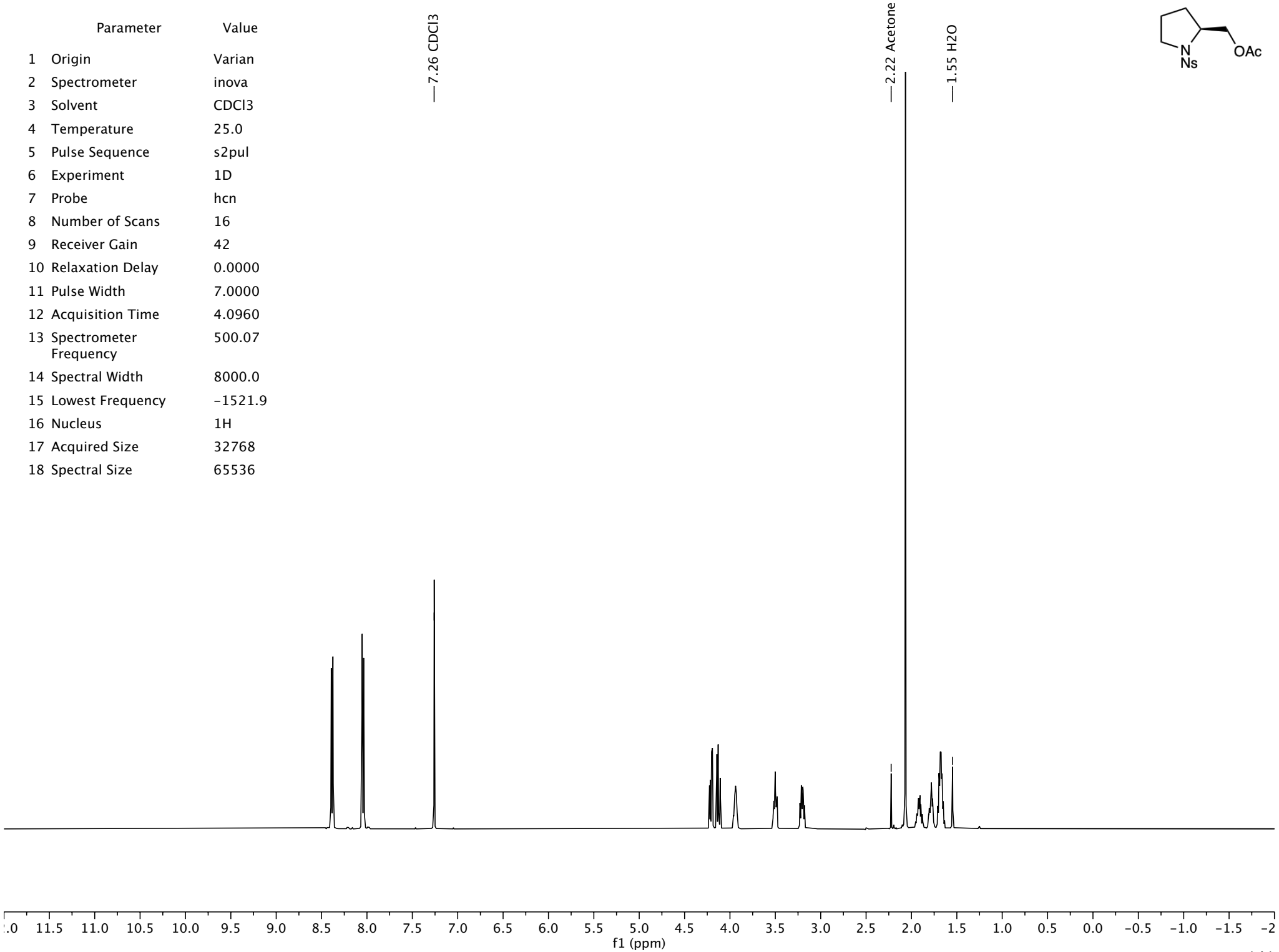
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1759.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



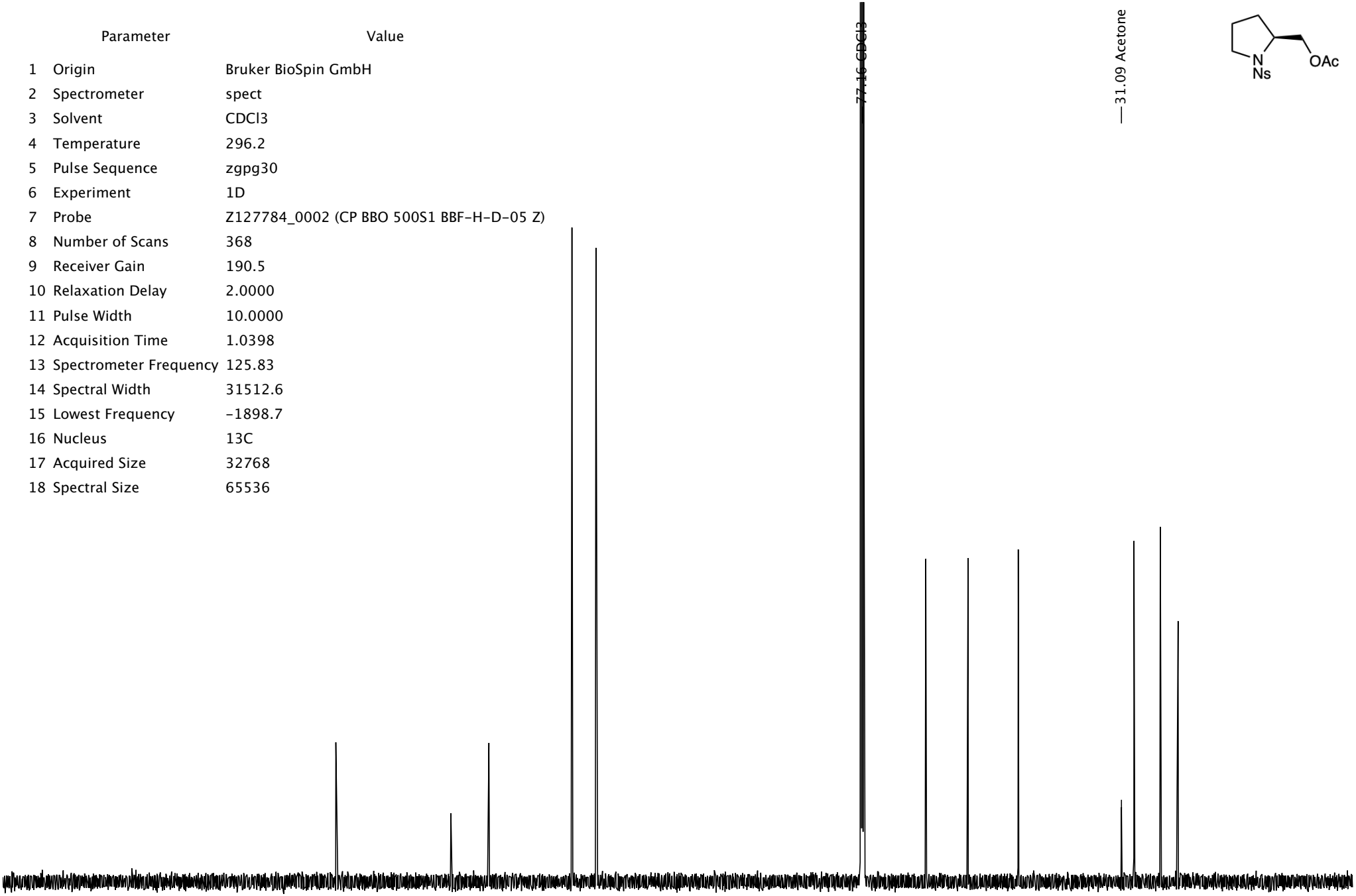
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	256
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



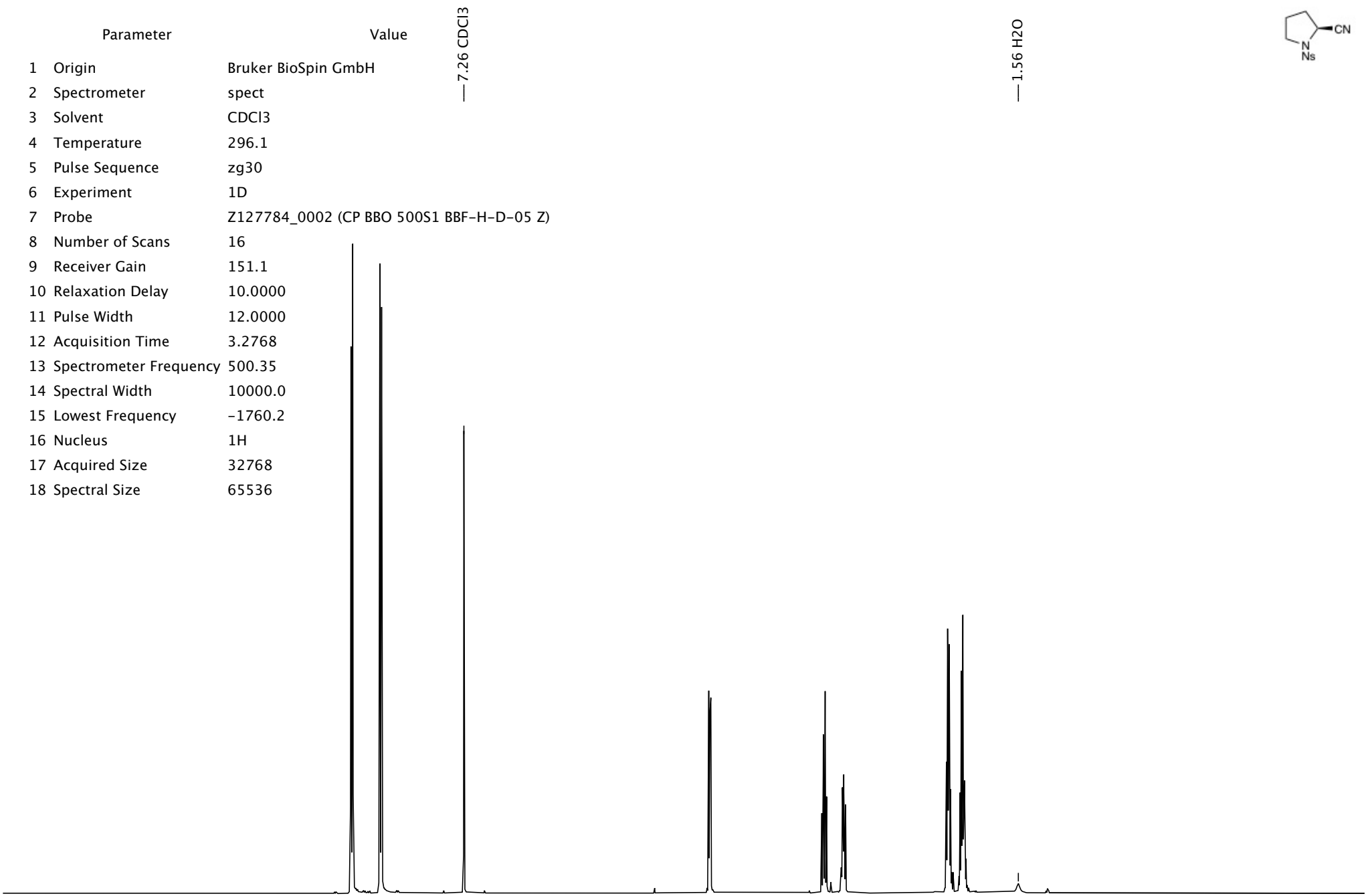
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



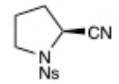
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.7
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	151.1
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1760.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

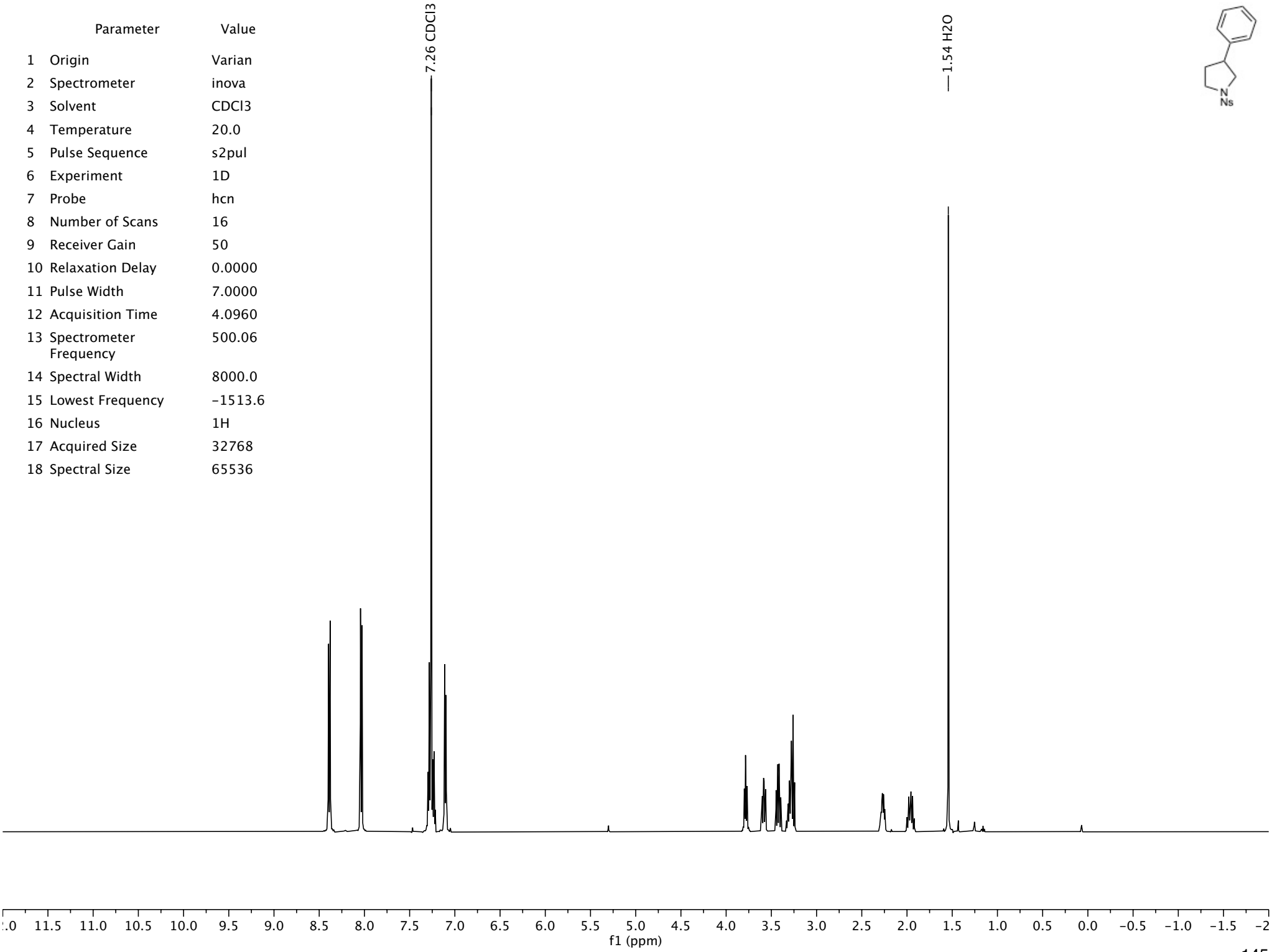


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

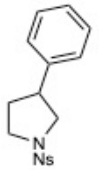


77.16 CDCl3

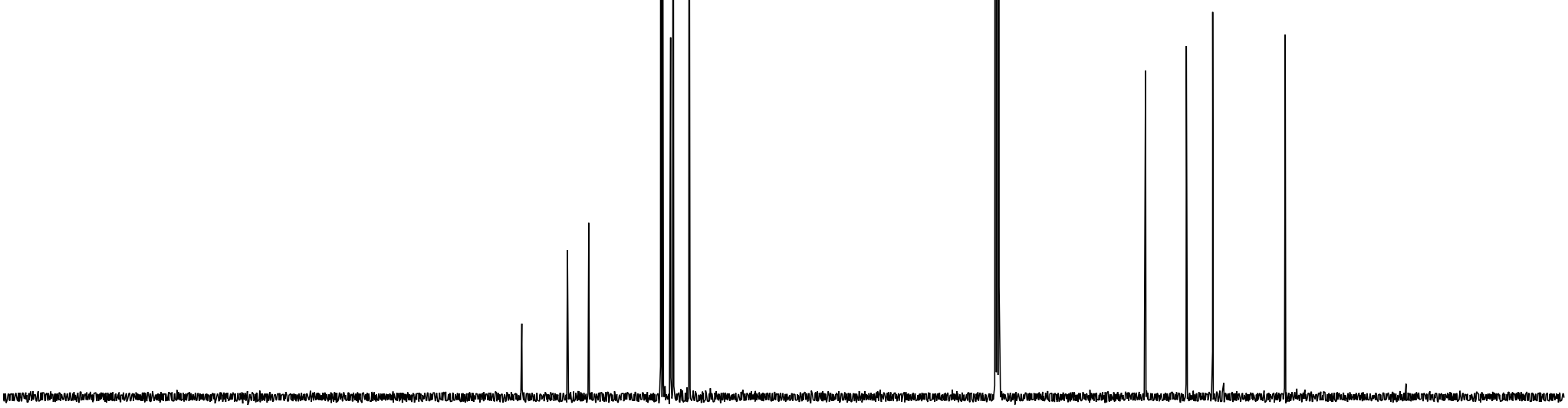
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	50
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

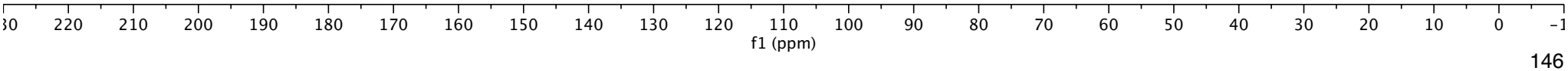


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	256
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

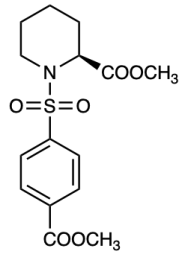


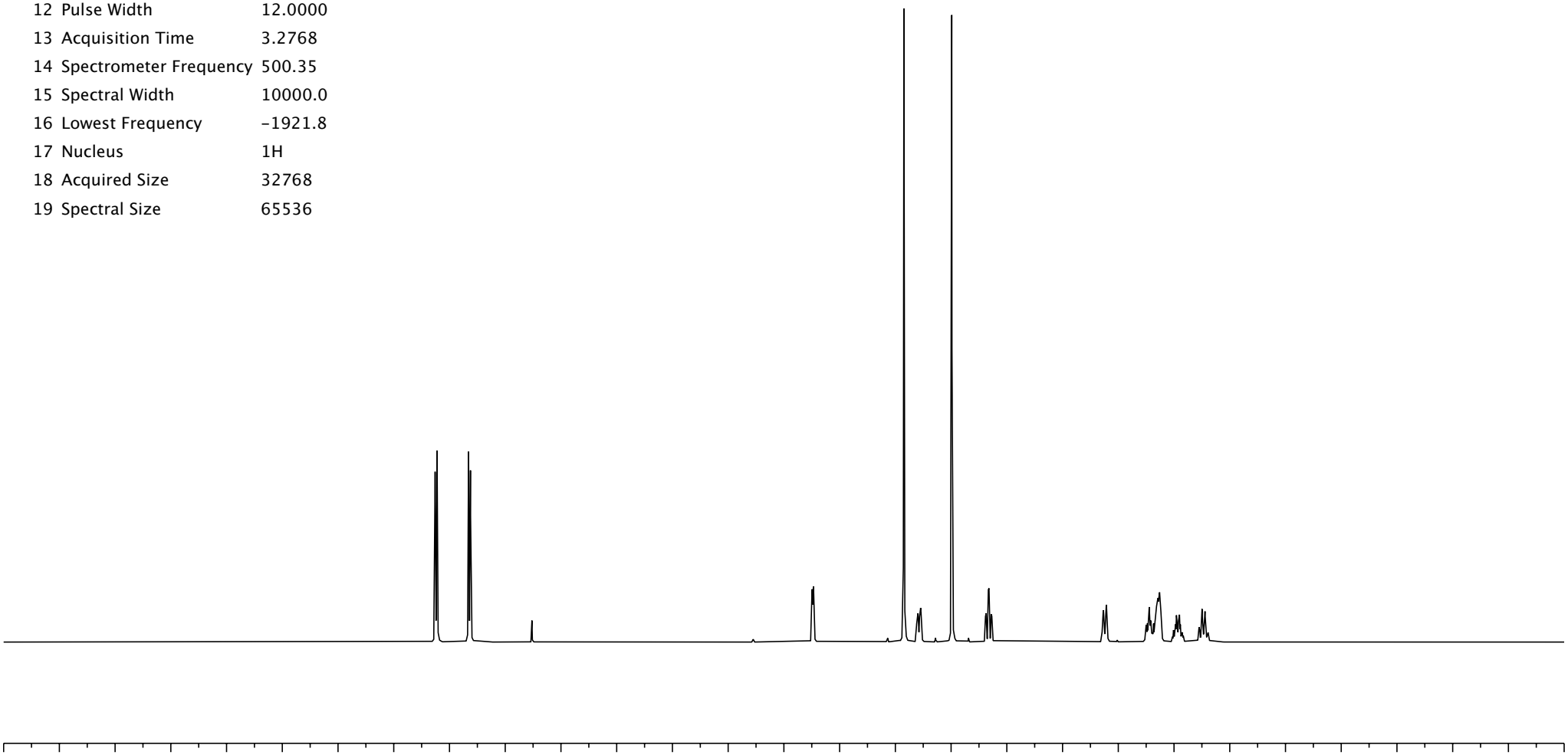
77.16 CDCl3

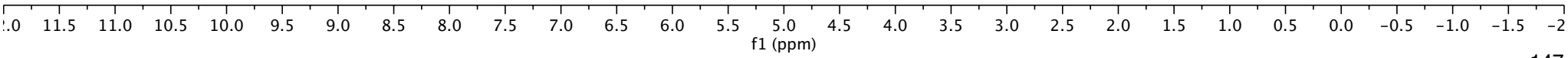




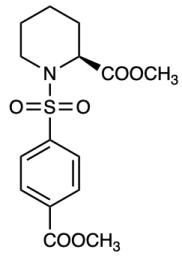
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1921.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

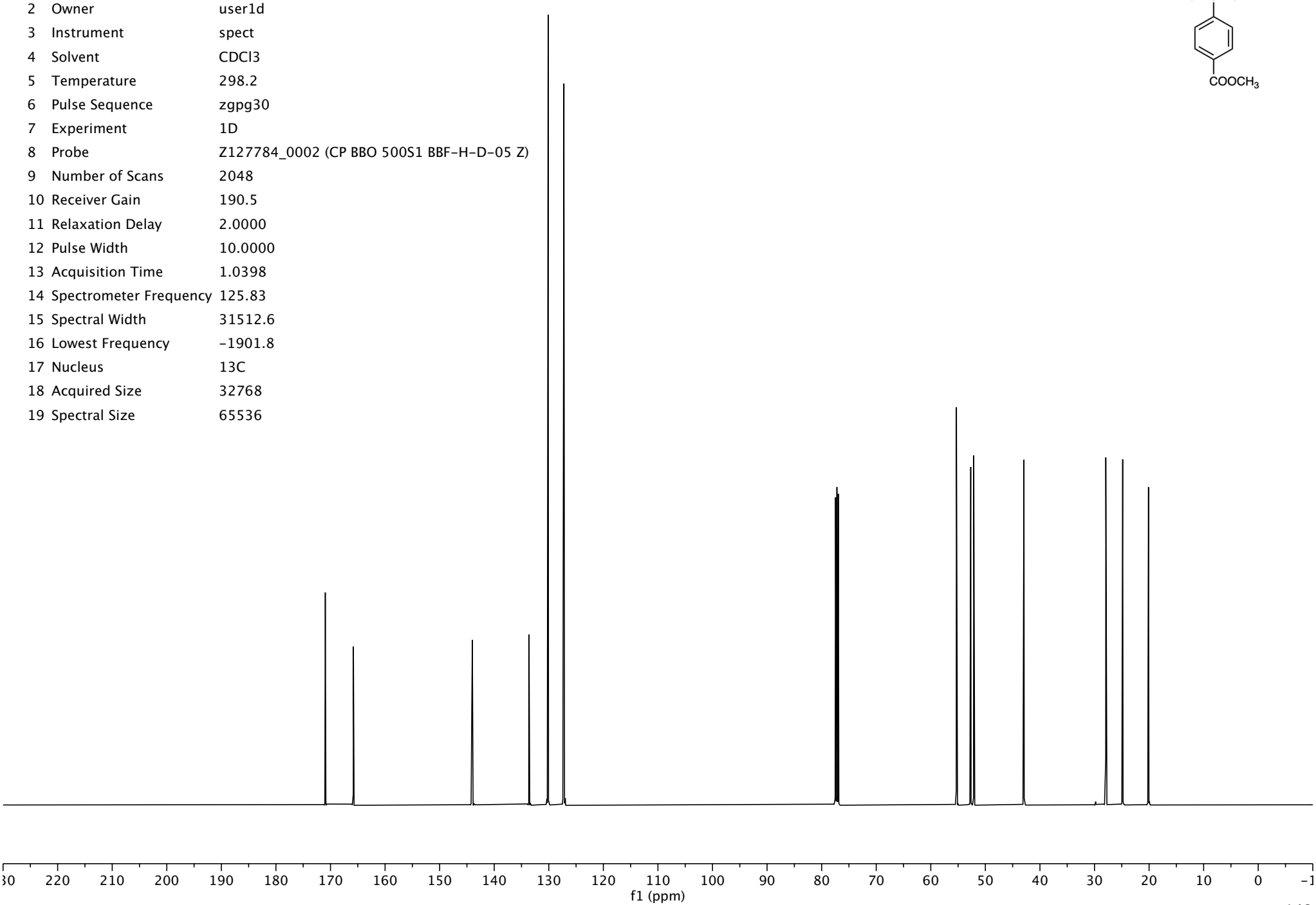


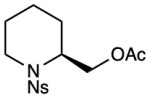




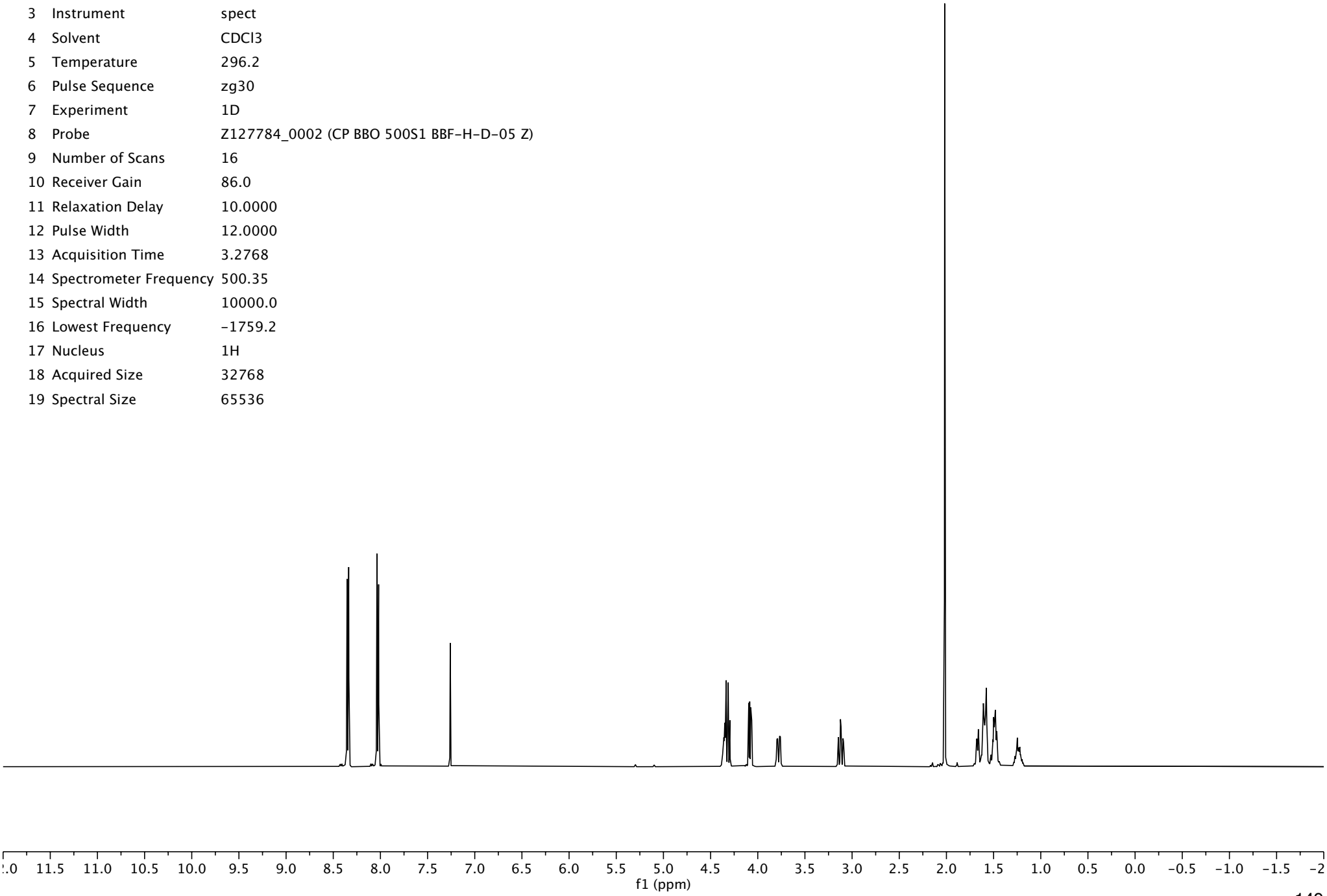
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1901.8
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

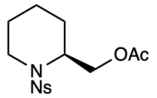




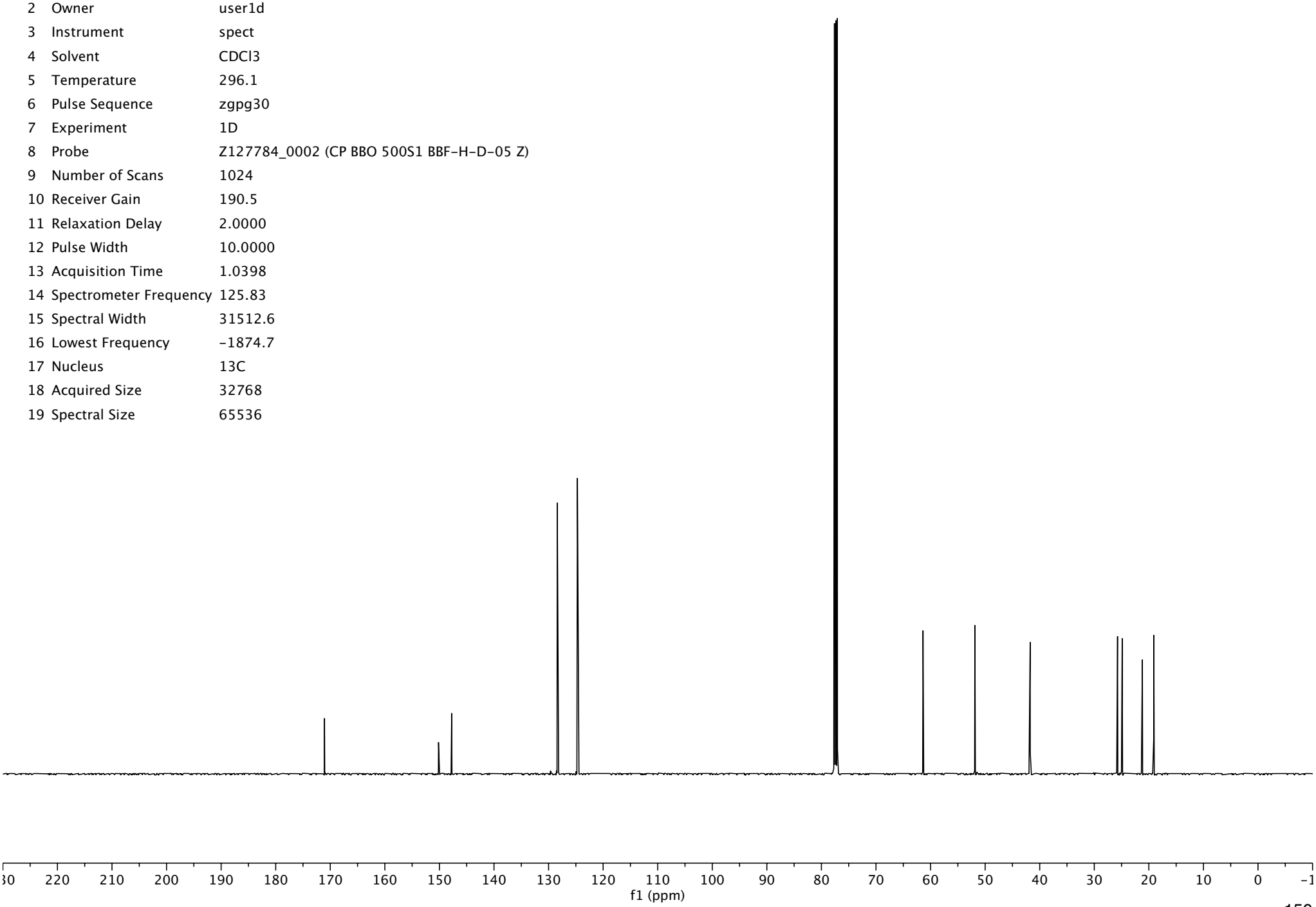


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



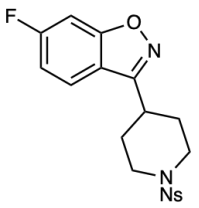


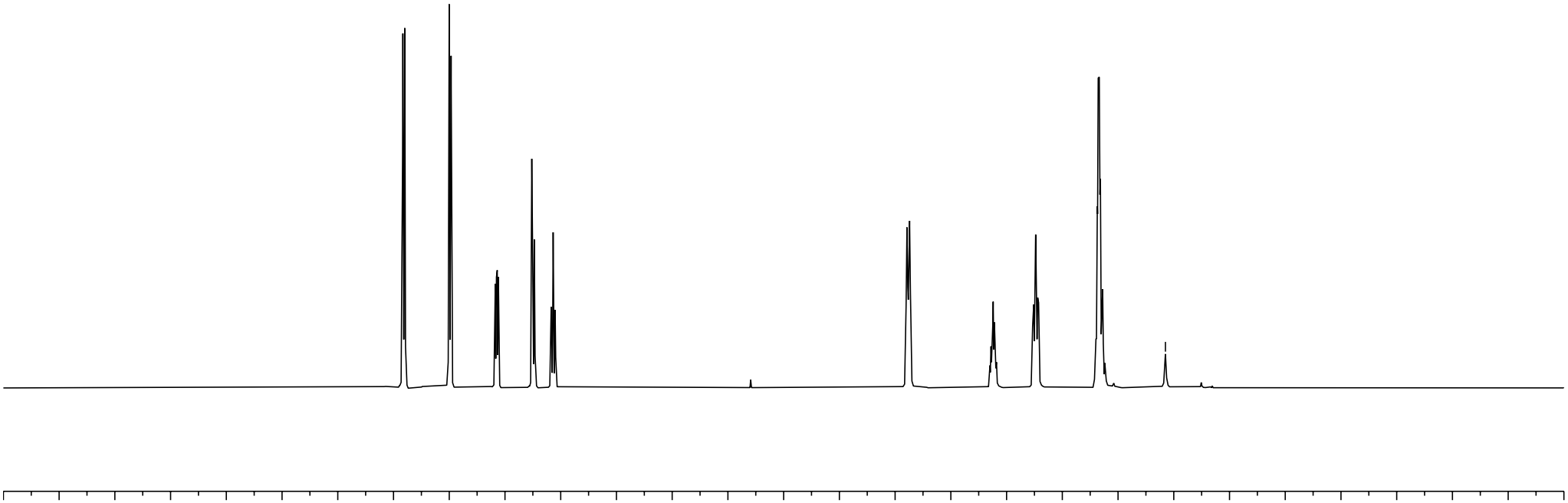
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

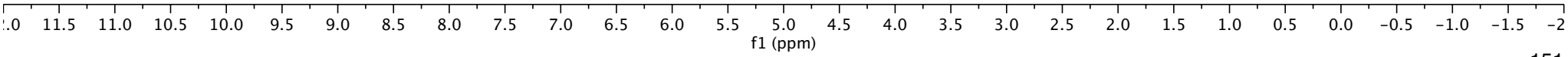


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	94.3
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1921.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

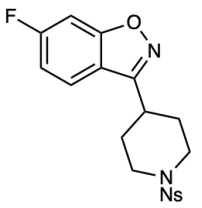
1.57 H2O



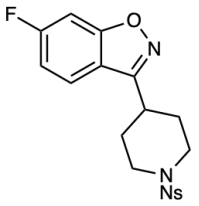


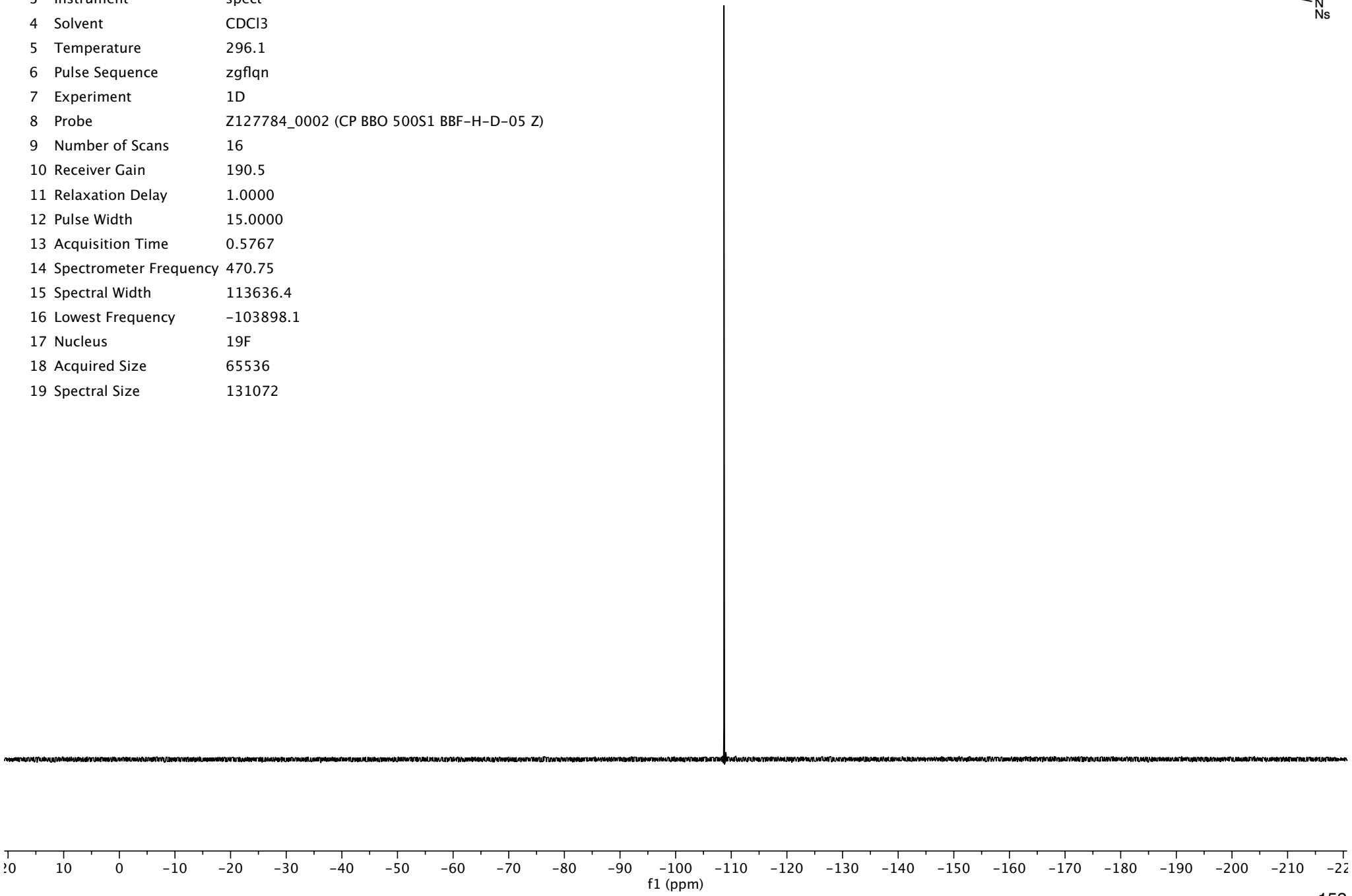


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

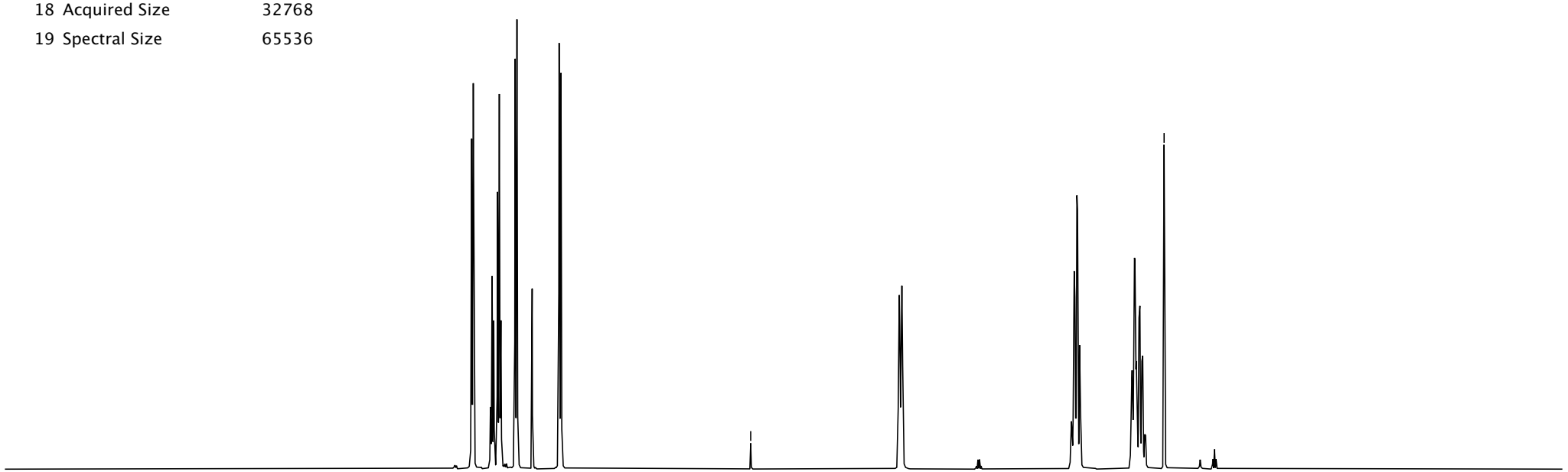


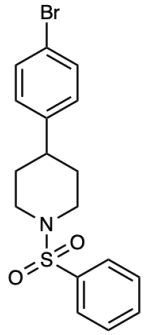
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

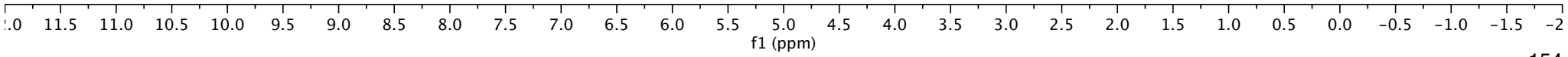




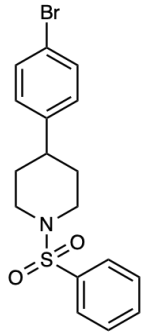
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

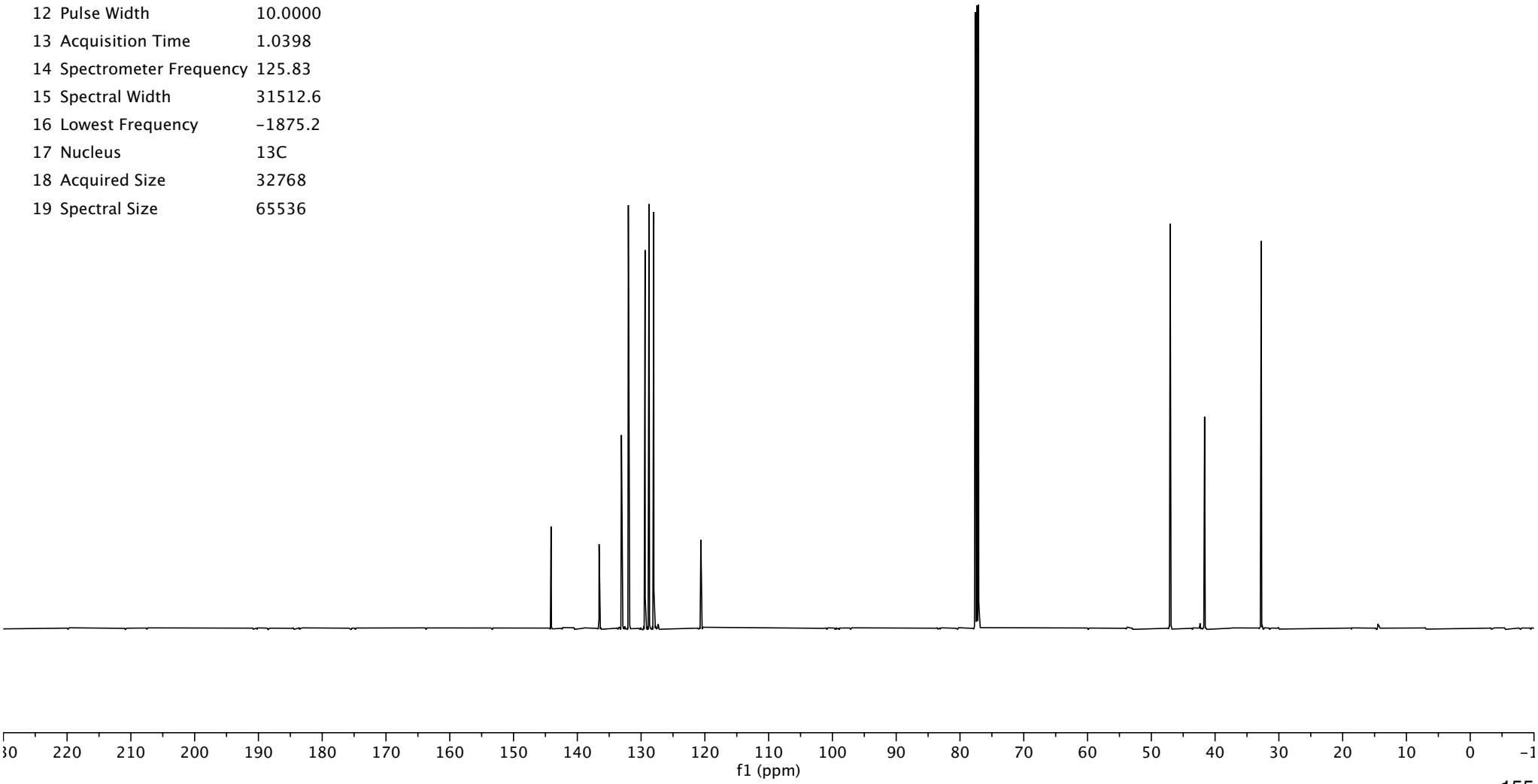


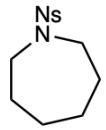




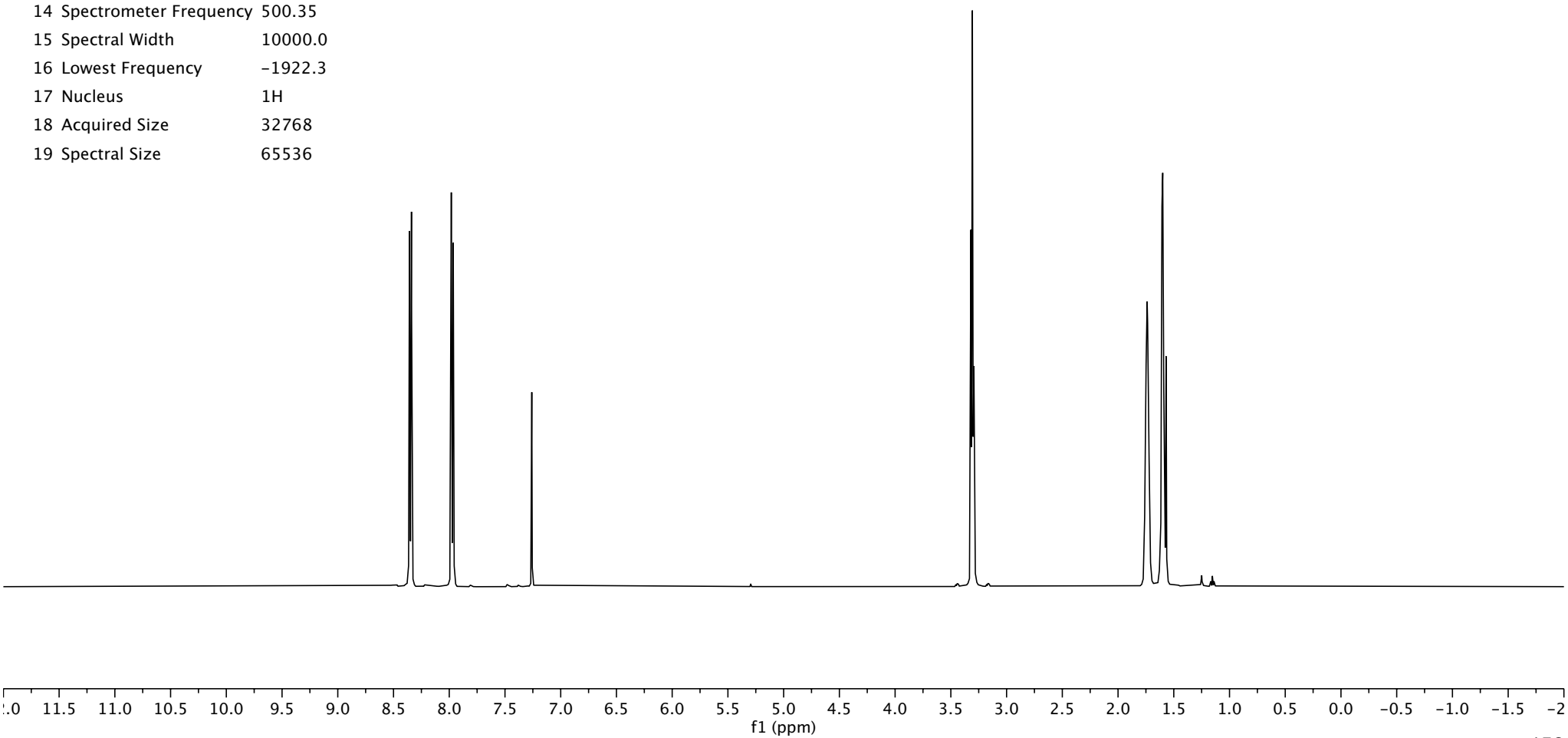
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1875.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



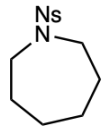


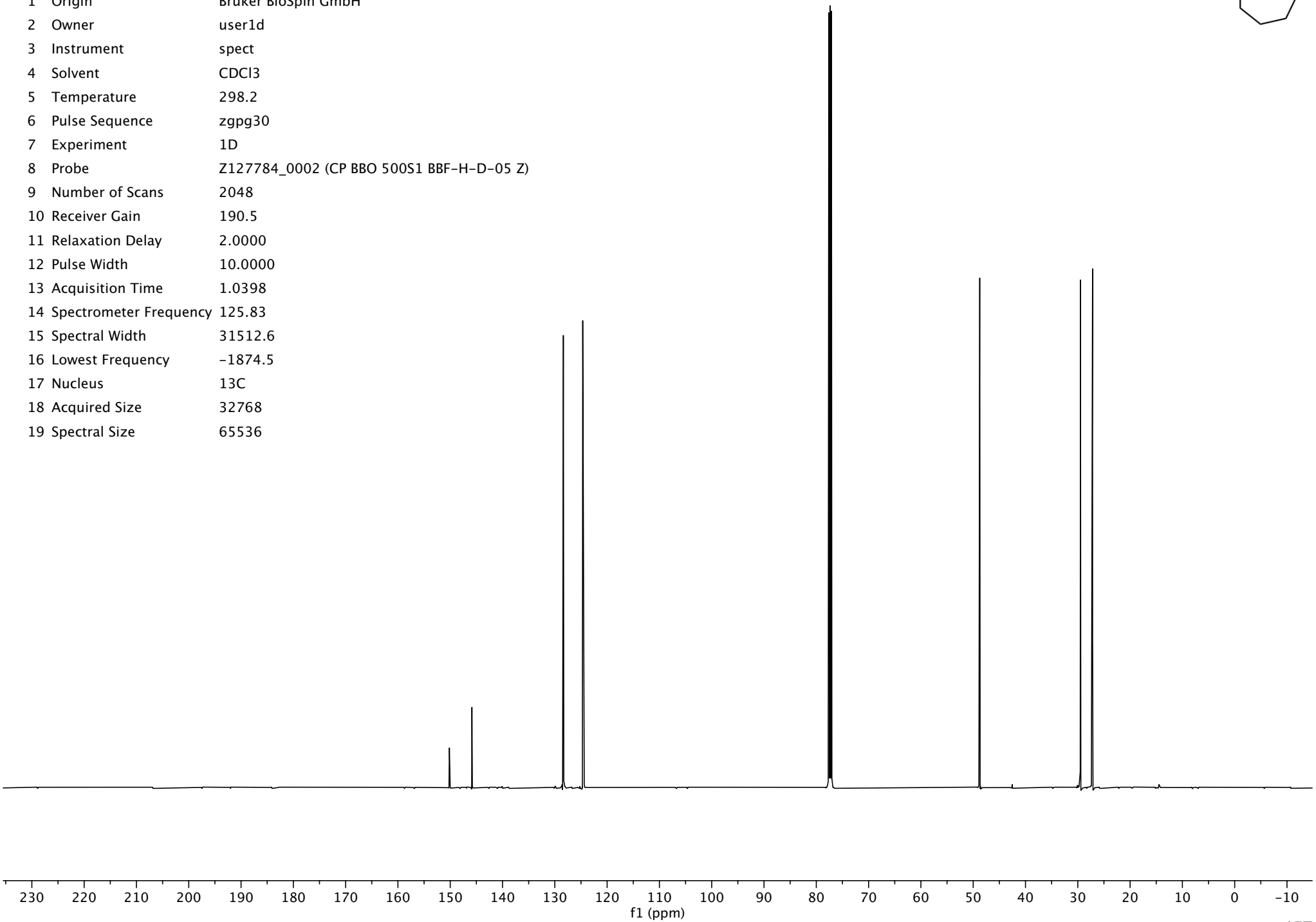


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

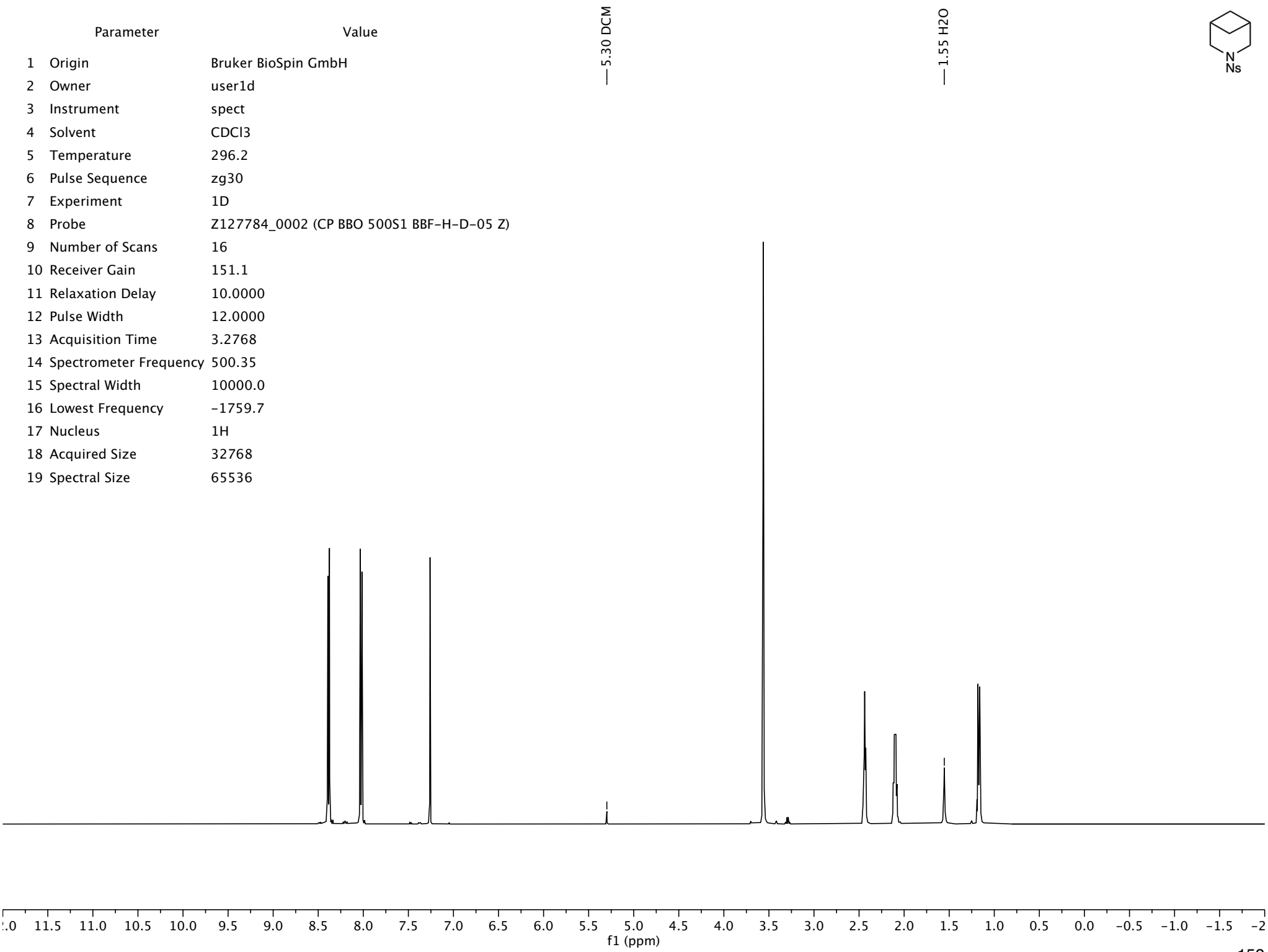


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

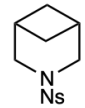


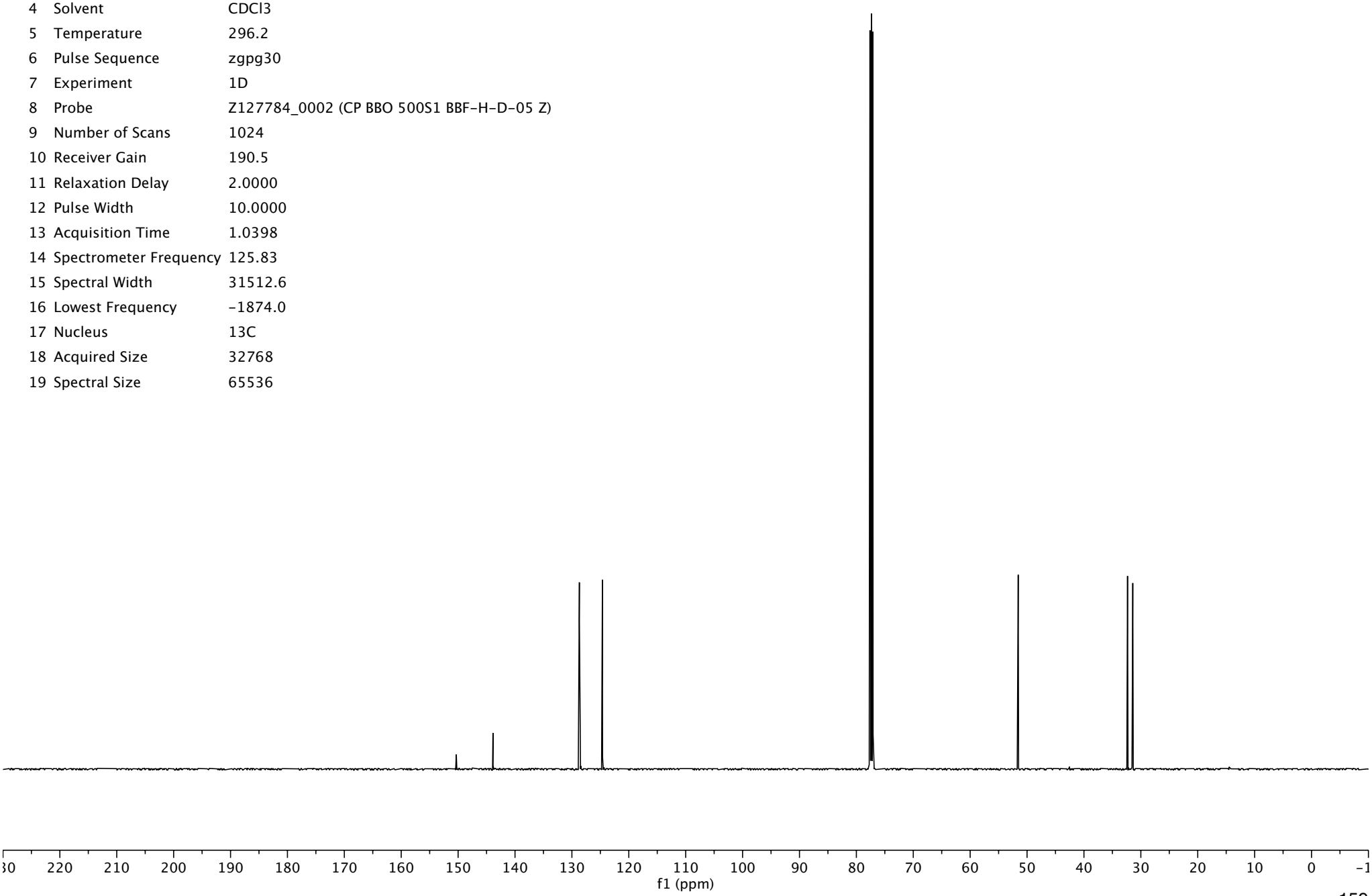


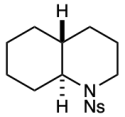
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	151.1
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



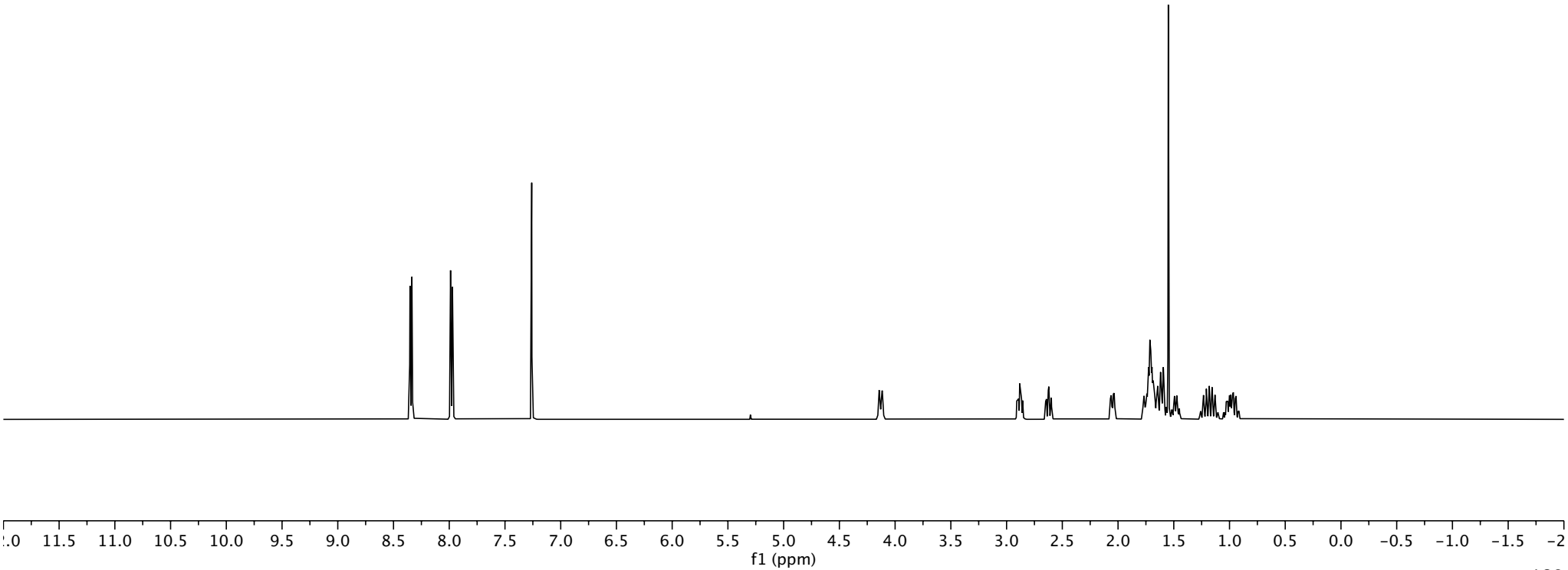
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



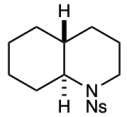




	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	122.8
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



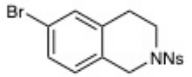
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	4096
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1872.8
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

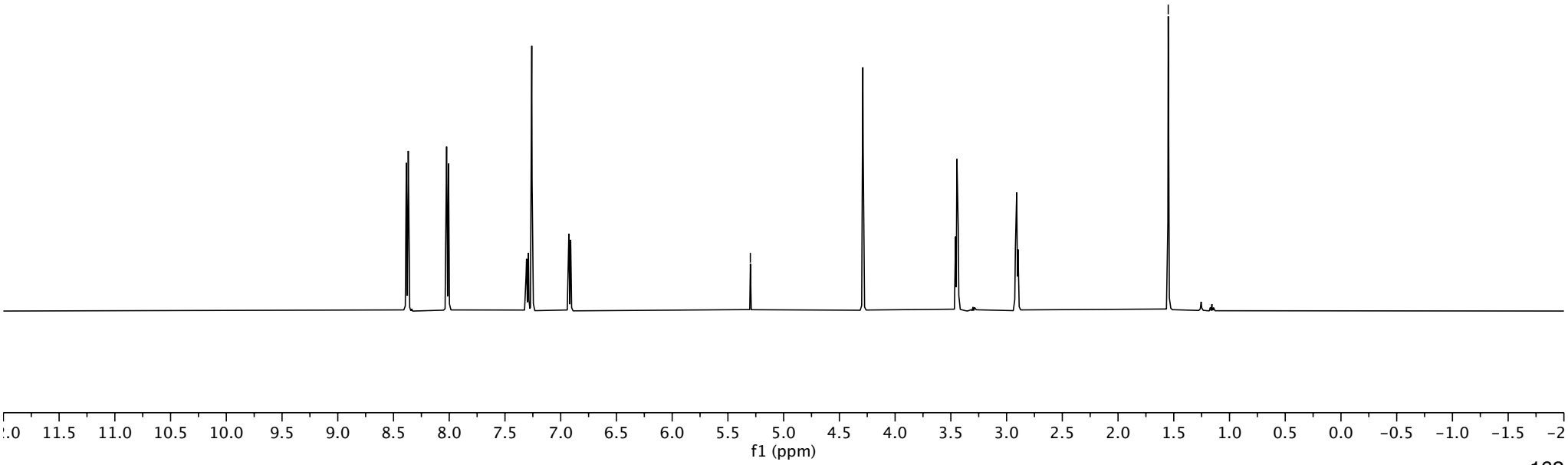


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	151.1
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

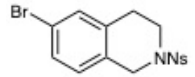
5.30 DCM

1.55 H2O

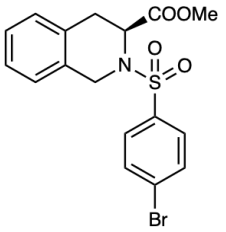


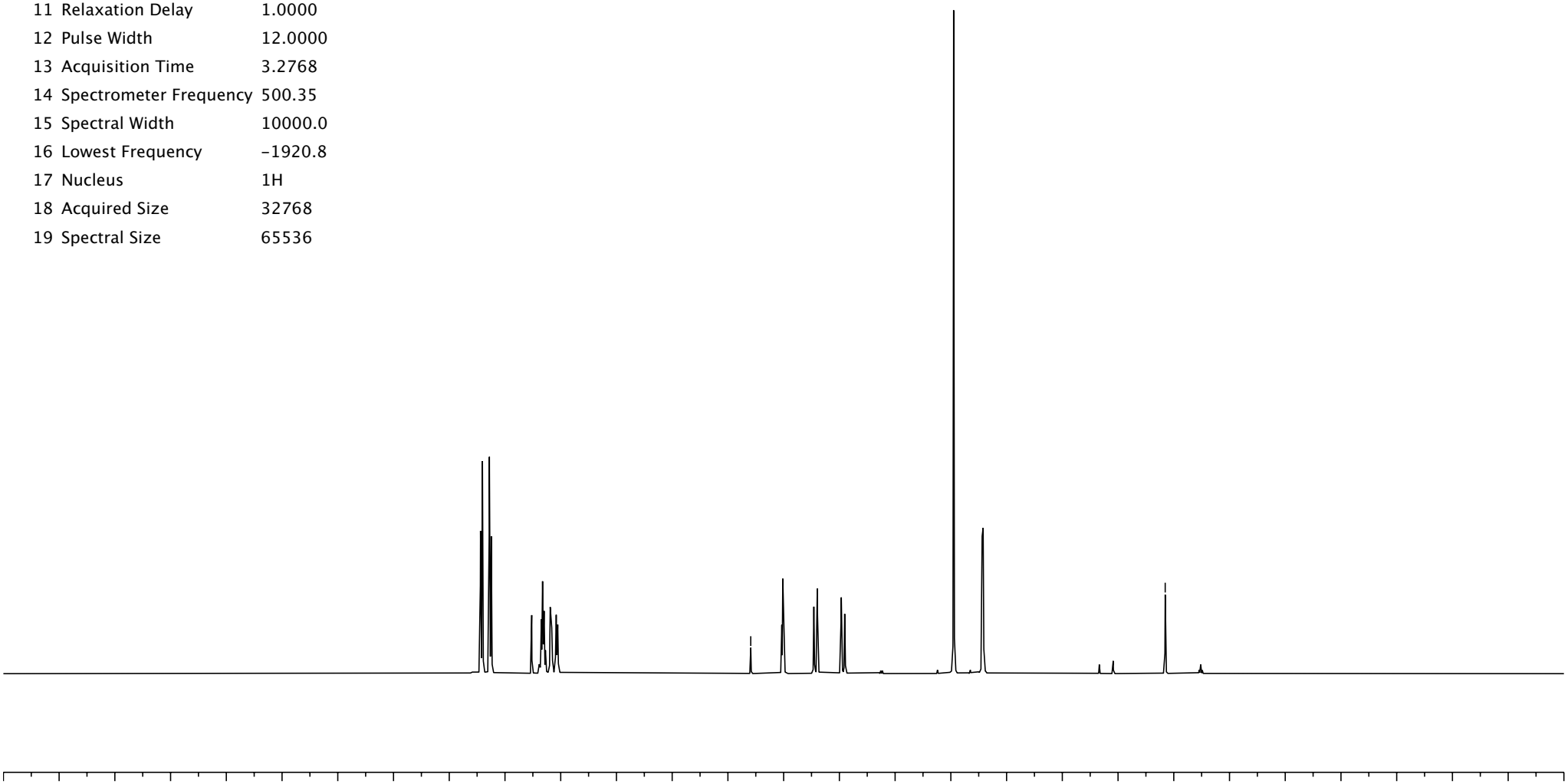


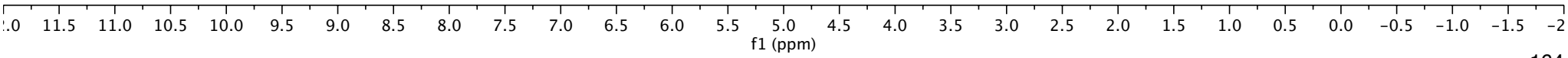
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1872.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

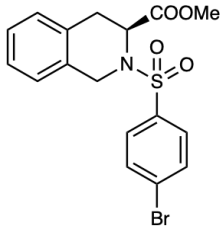


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	1.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

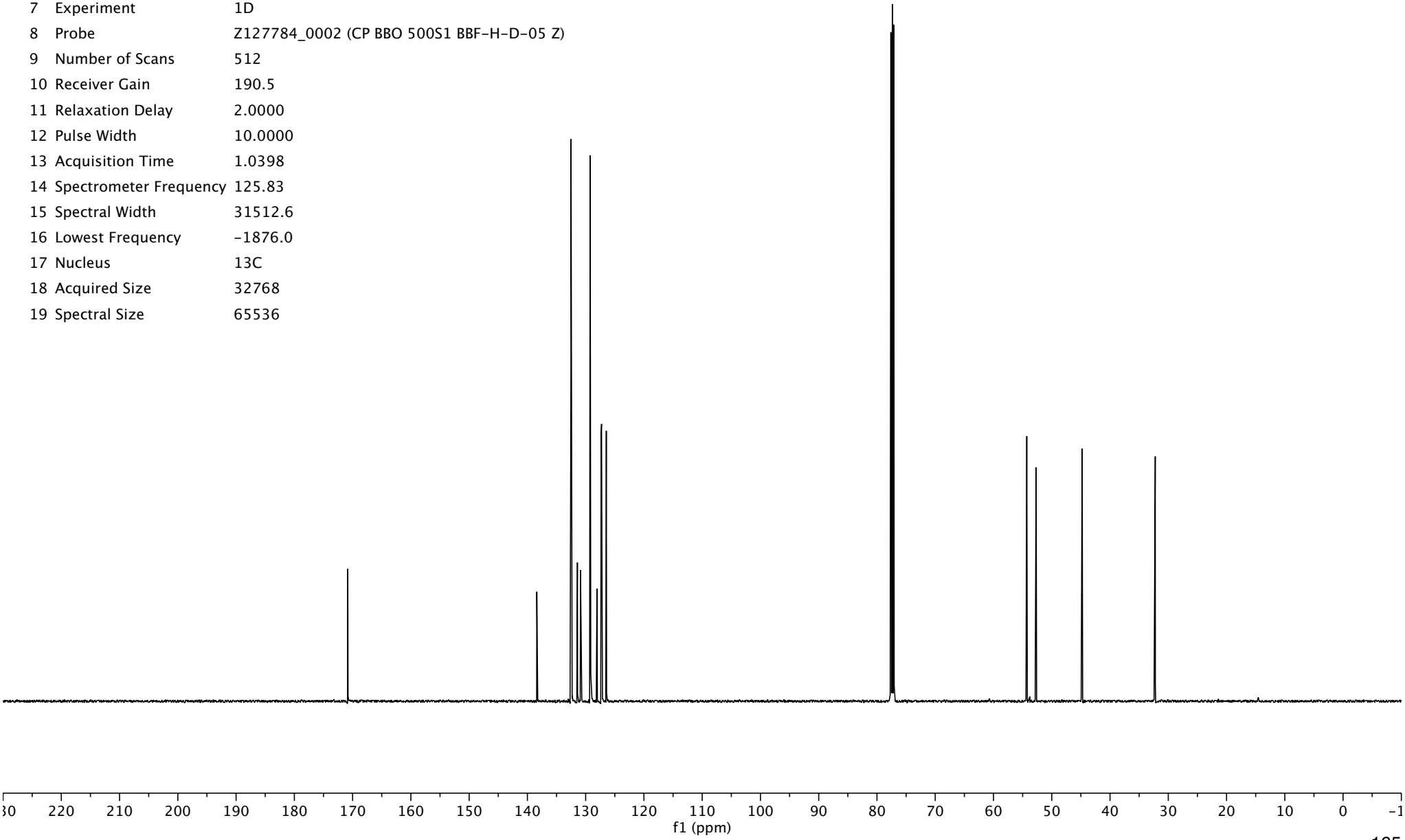






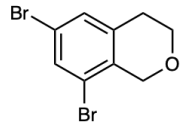


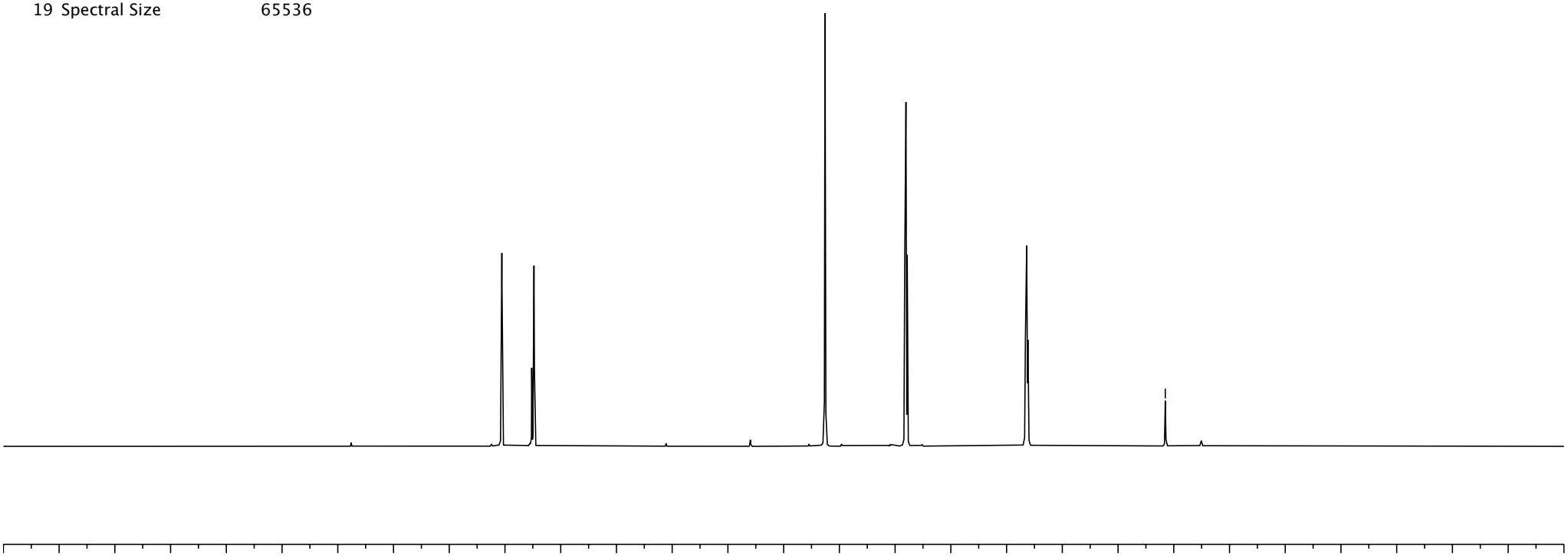
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1876.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

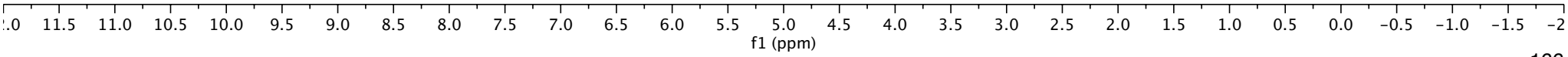


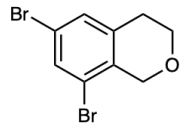
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1700.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

1.58 H2O

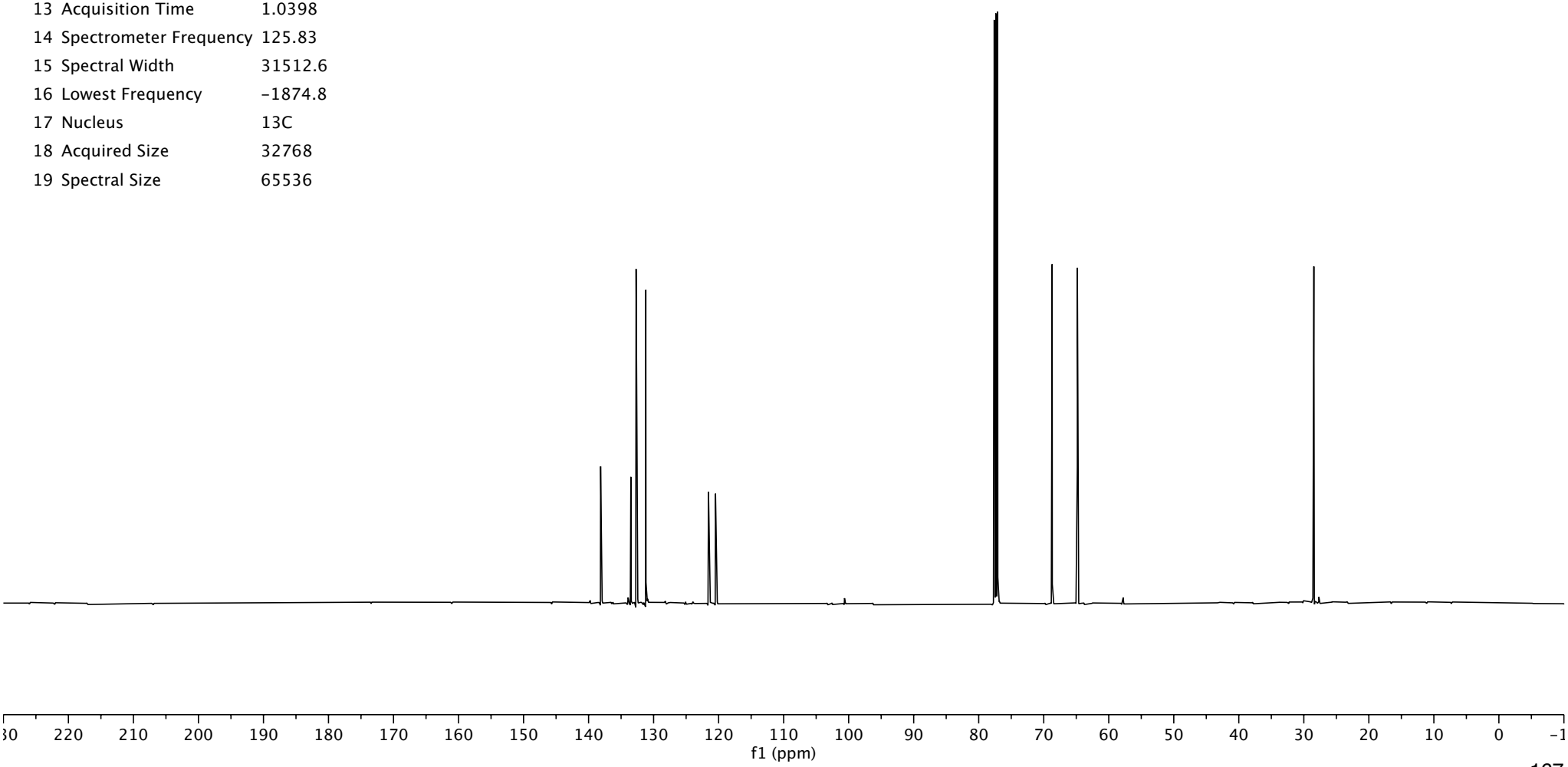


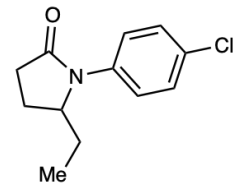




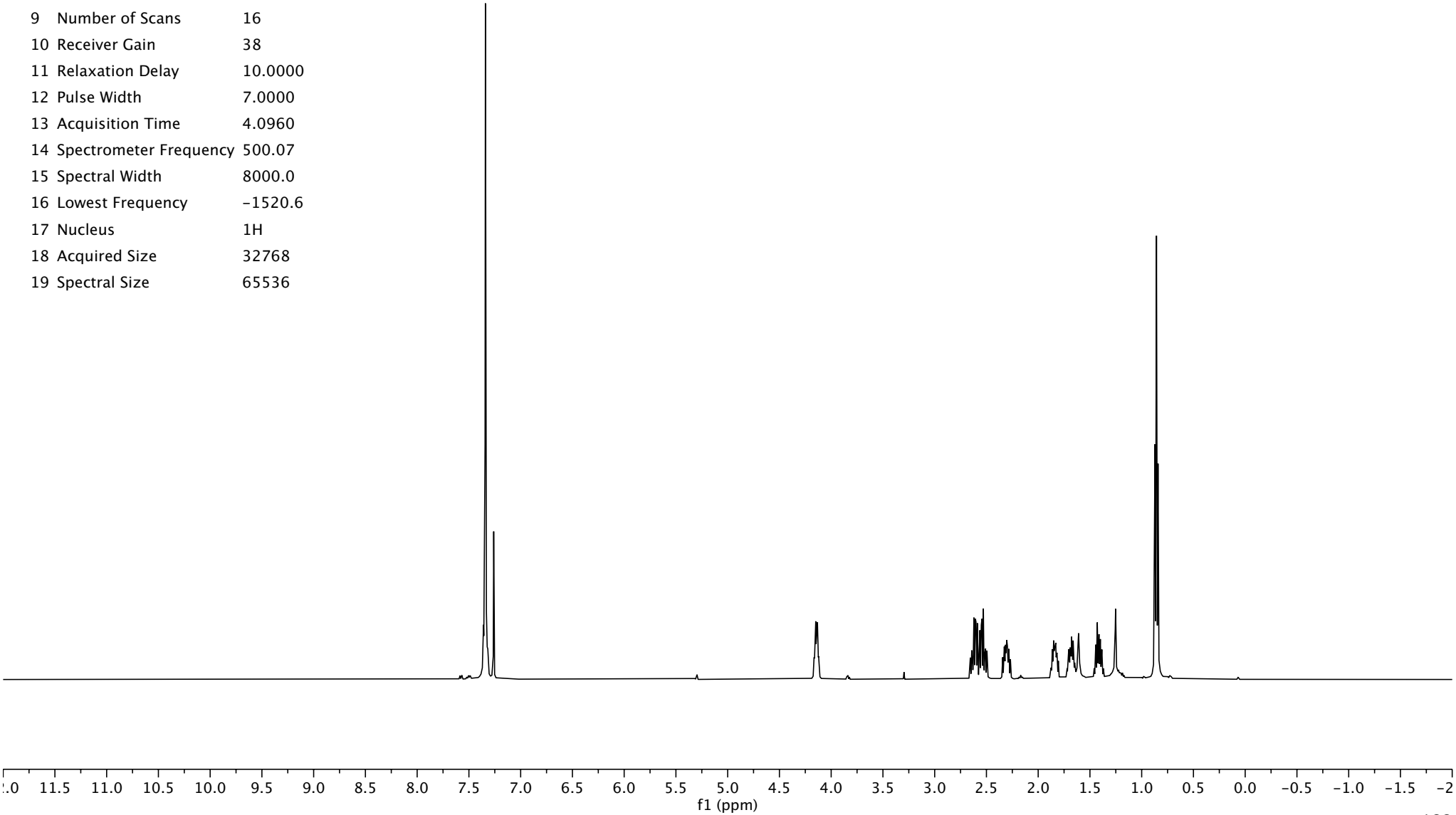


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.8
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

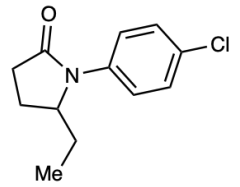


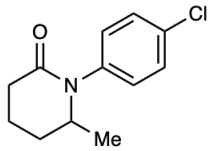


	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	16
10	Receiver Gain	38
11	Relaxation Delay	10.0000
12	Pulse Width	7.0000
13	Acquisition Time	4.0960
14	Spectrometer Frequency	500.07
15	Spectral Width	8000.0
16	Lowest Frequency	-1520.6
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

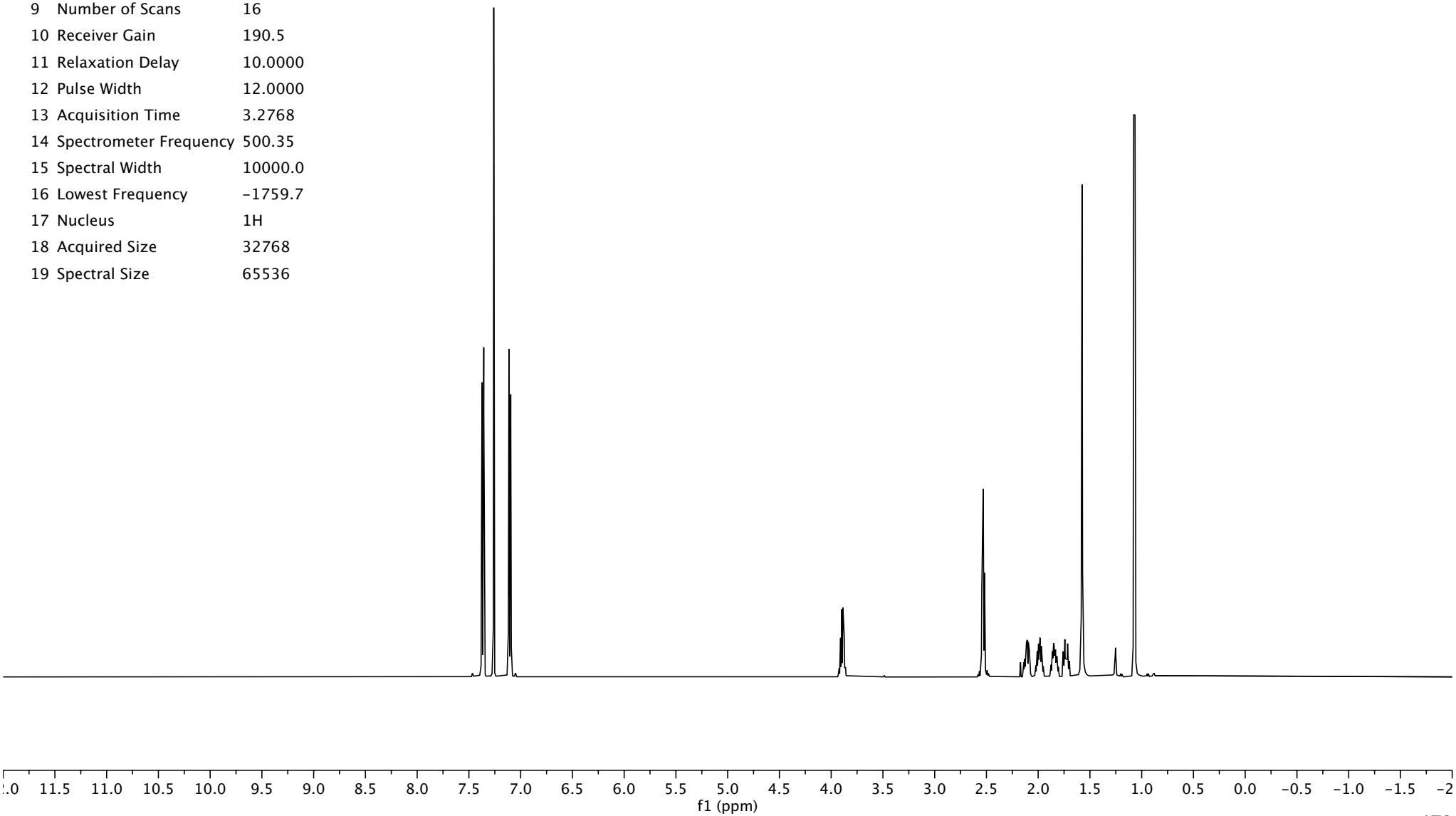


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1898.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

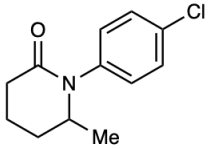




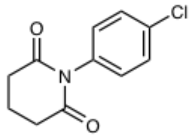
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

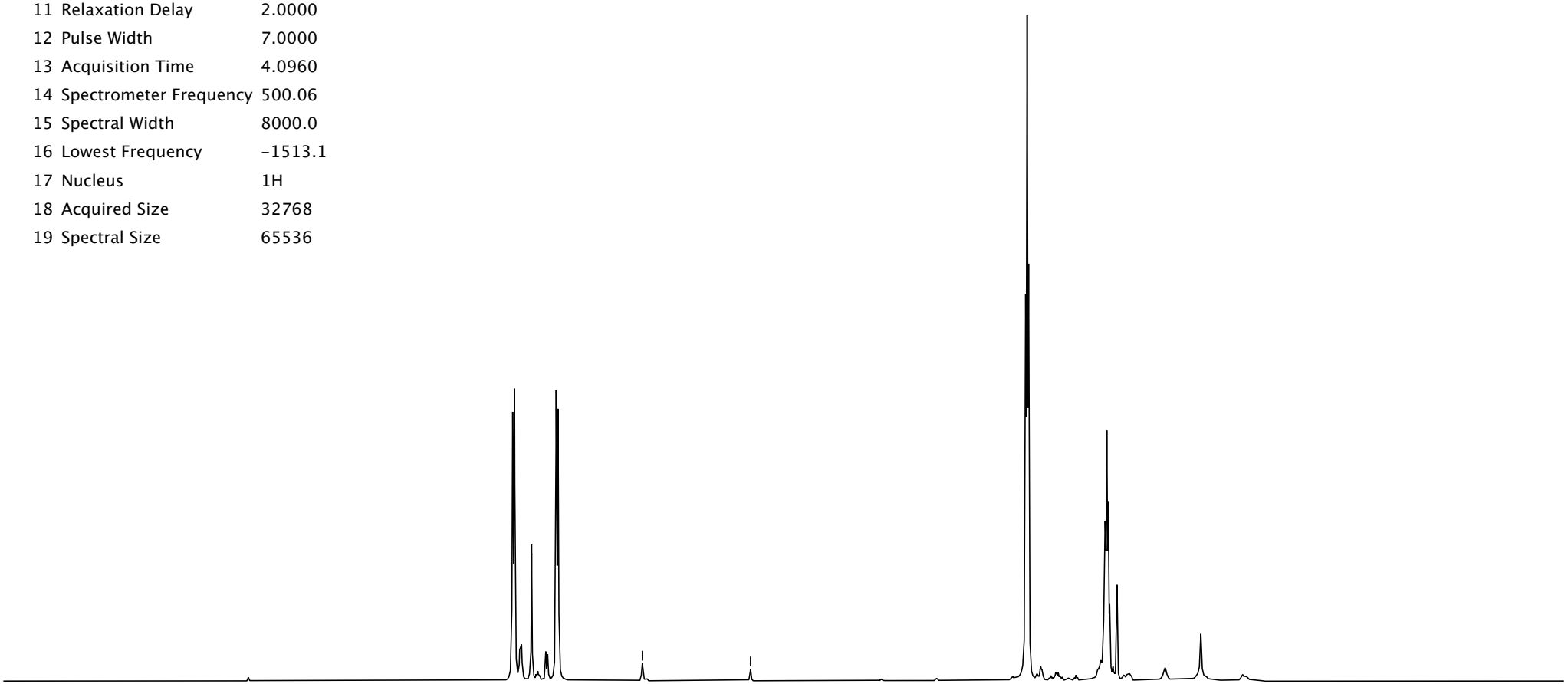


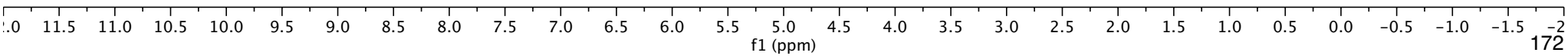
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1873.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



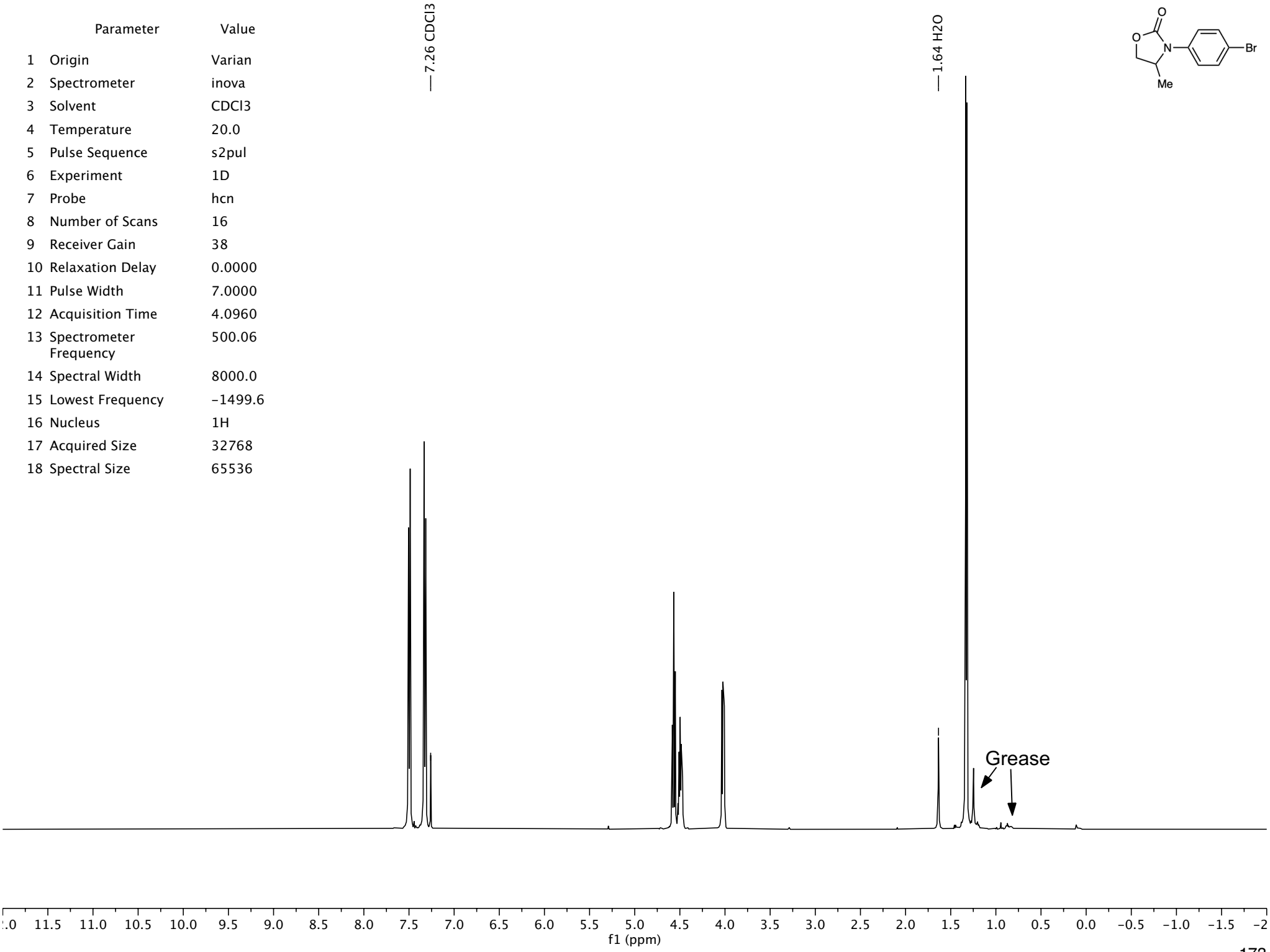
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	16
10	Receiver Gain	38
11	Relaxation Delay	2.0000
12	Pulse Width	7.0000
13	Acquisition Time	4.0960
14	Spectrometer Frequency	500.06
15	Spectral Width	8000.0
16	Lowest Frequency	-1513.1
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



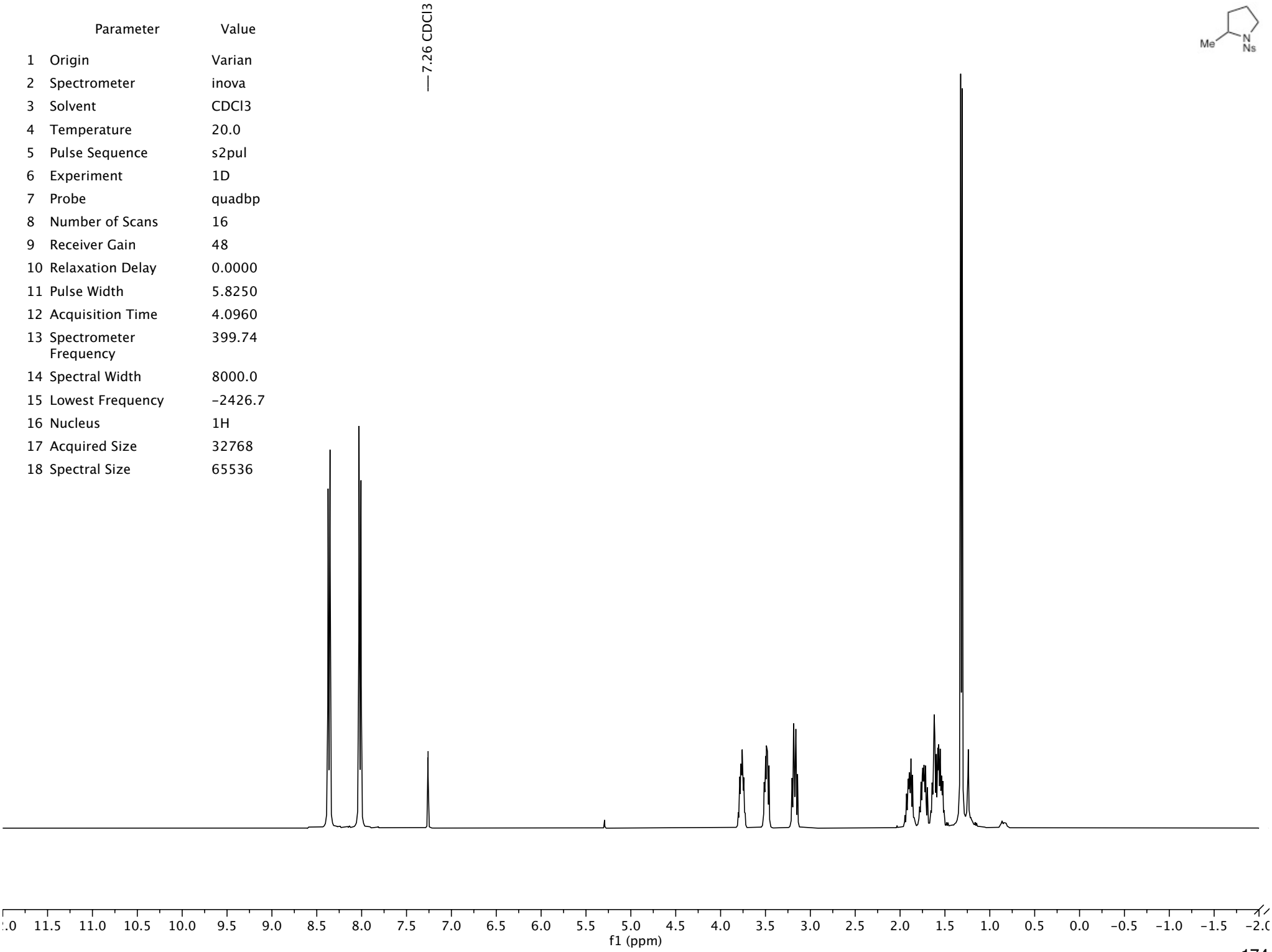




	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1499.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

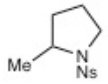


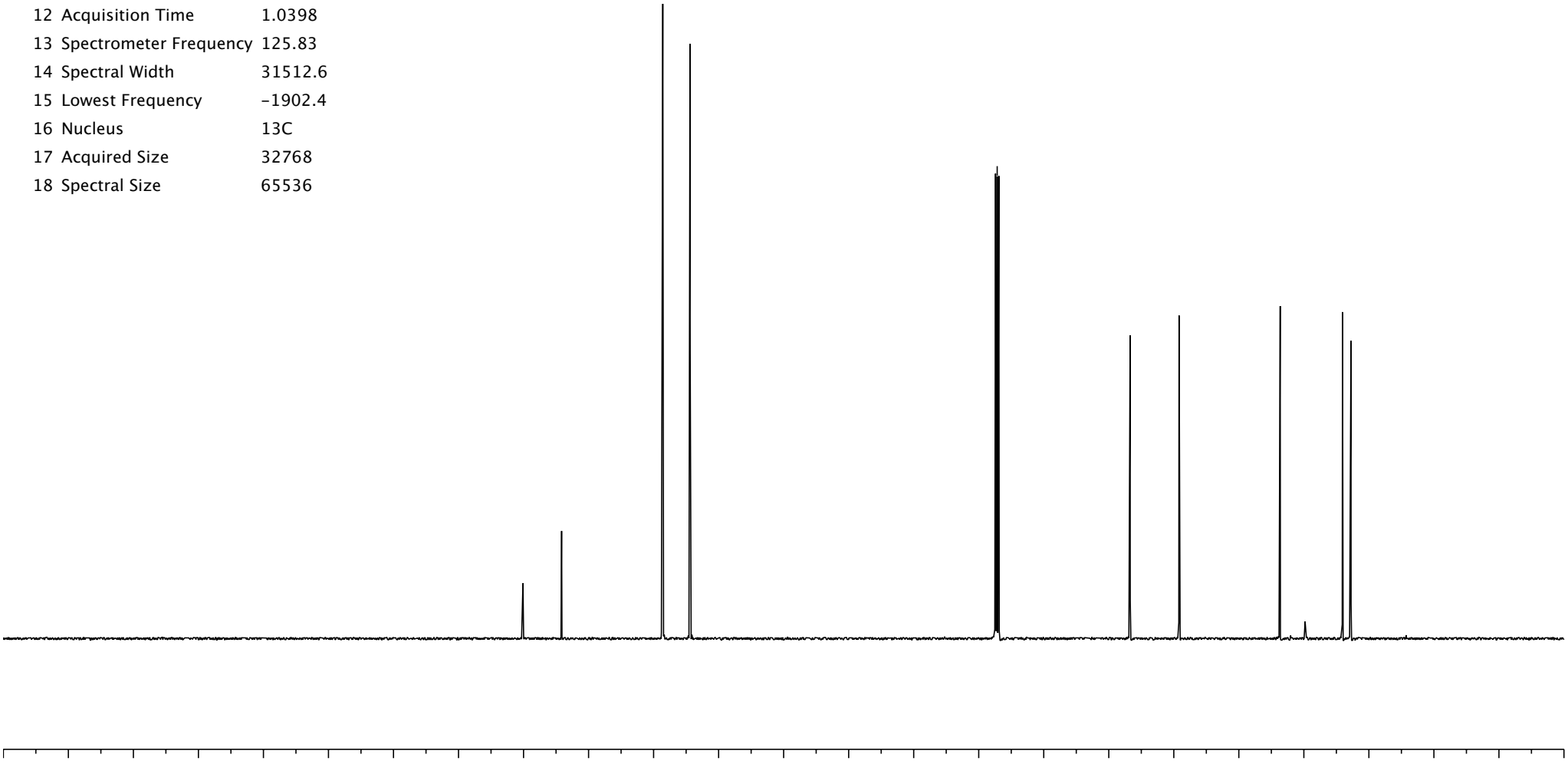
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2426.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

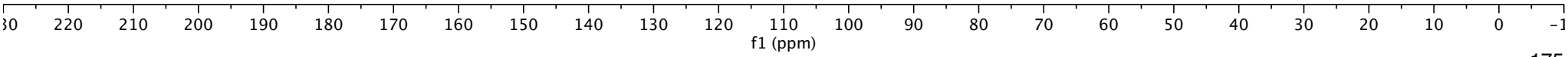


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	256
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1902.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

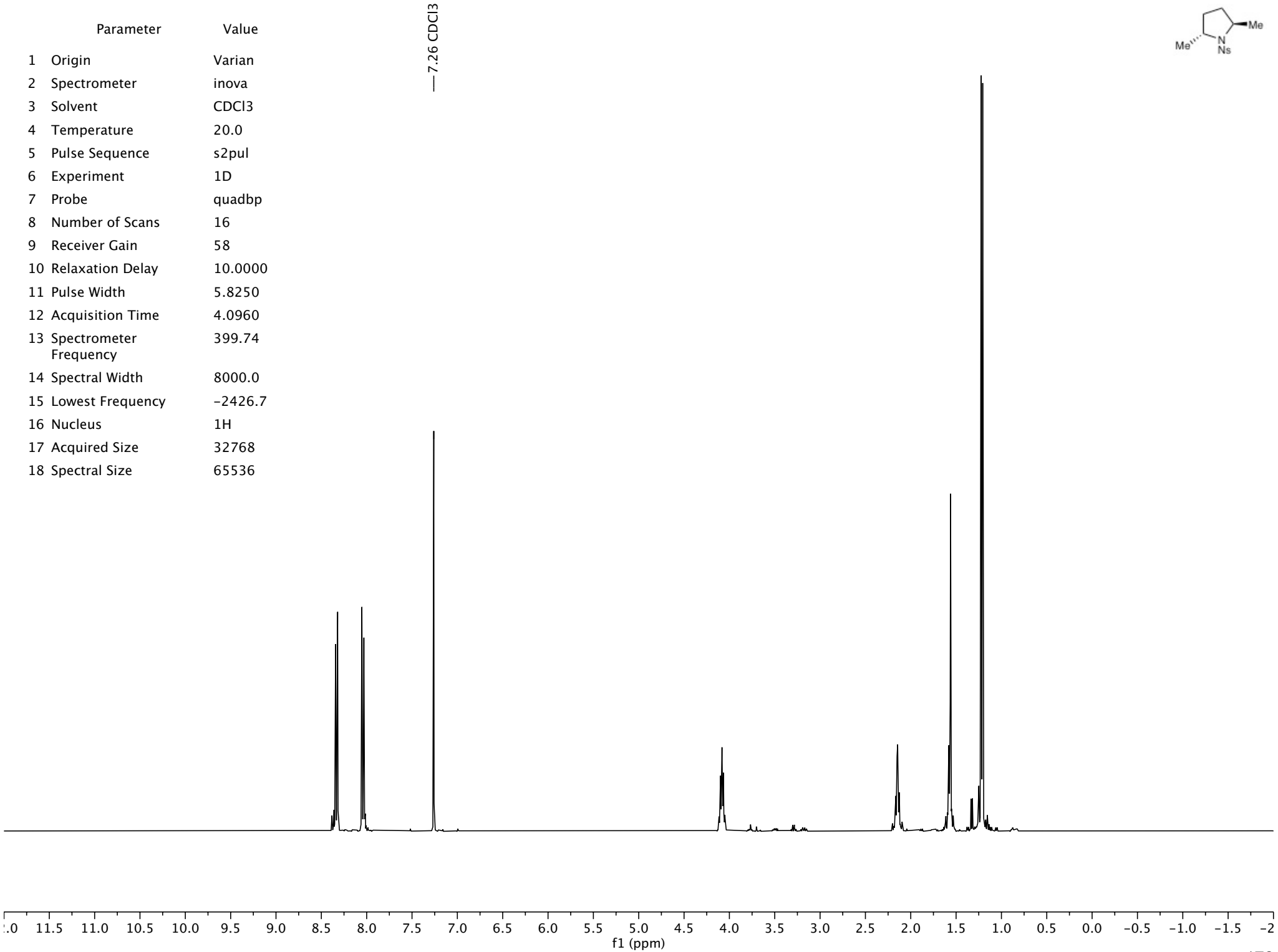
77.16 CDCl3



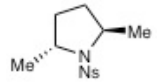




	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	58
10	Relaxation Delay	10.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2426.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	256
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



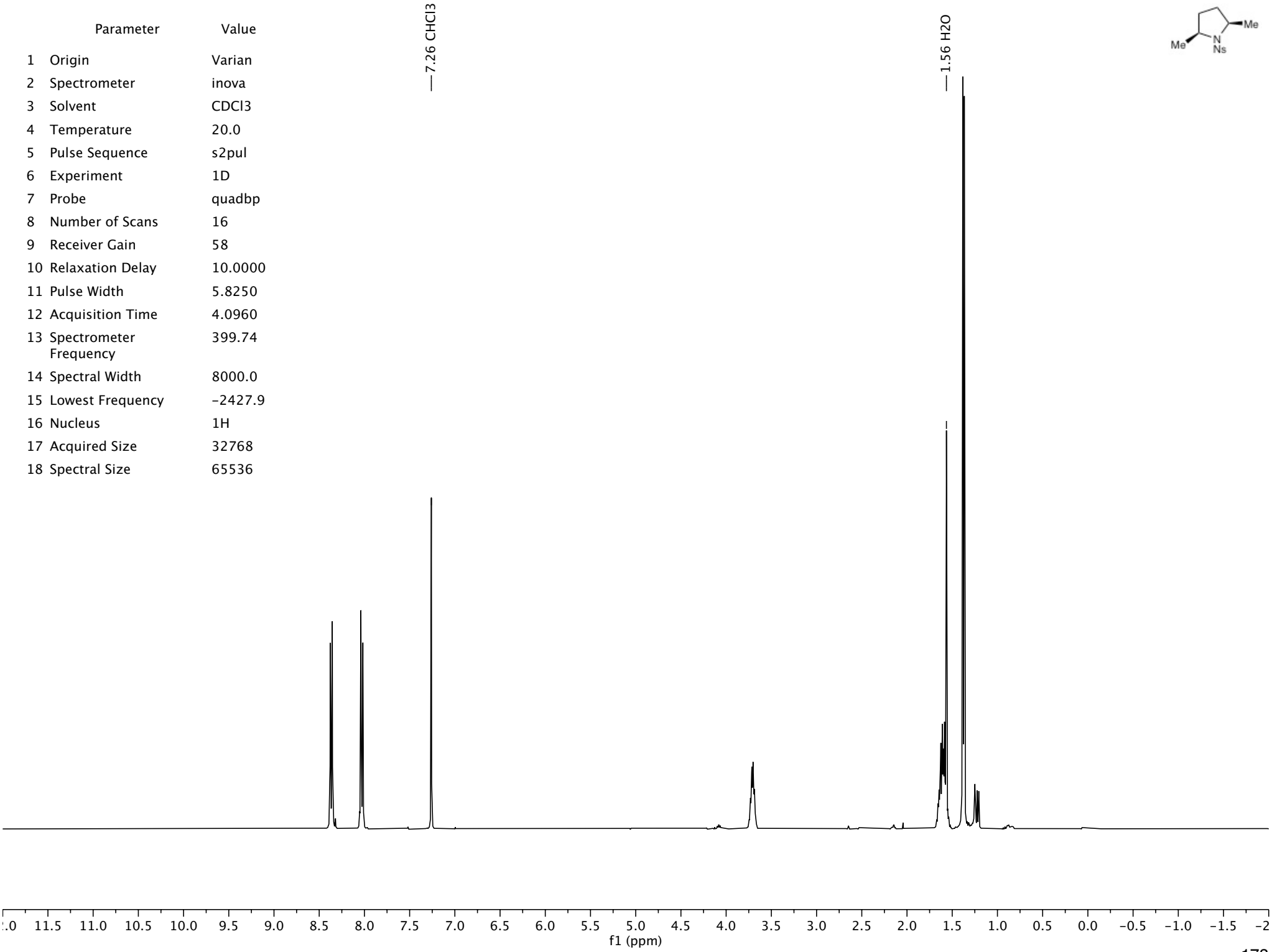
77.16 CDCl3

syn prod

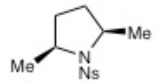
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

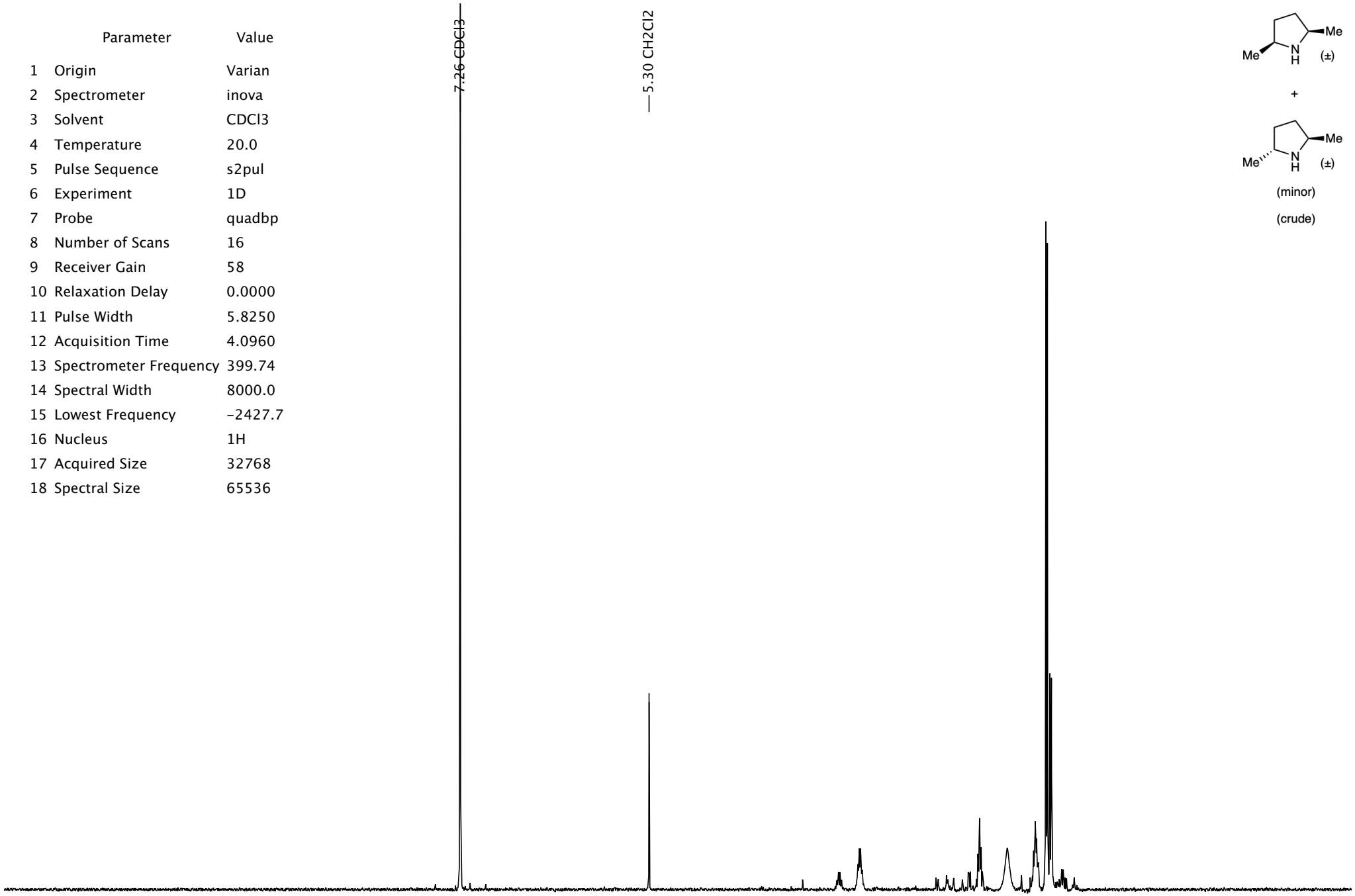
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	58
10	Relaxation Delay	10.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



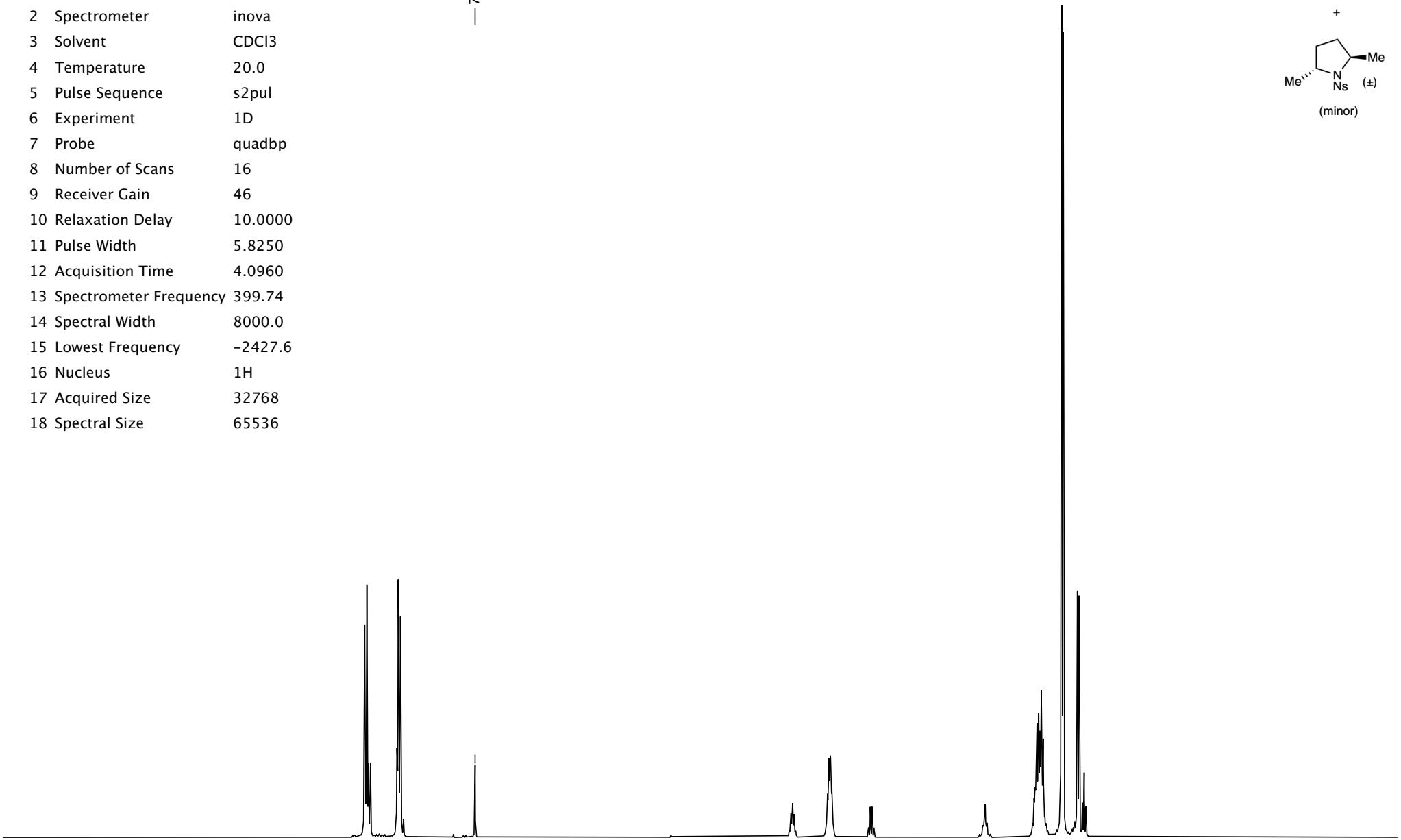
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	256
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

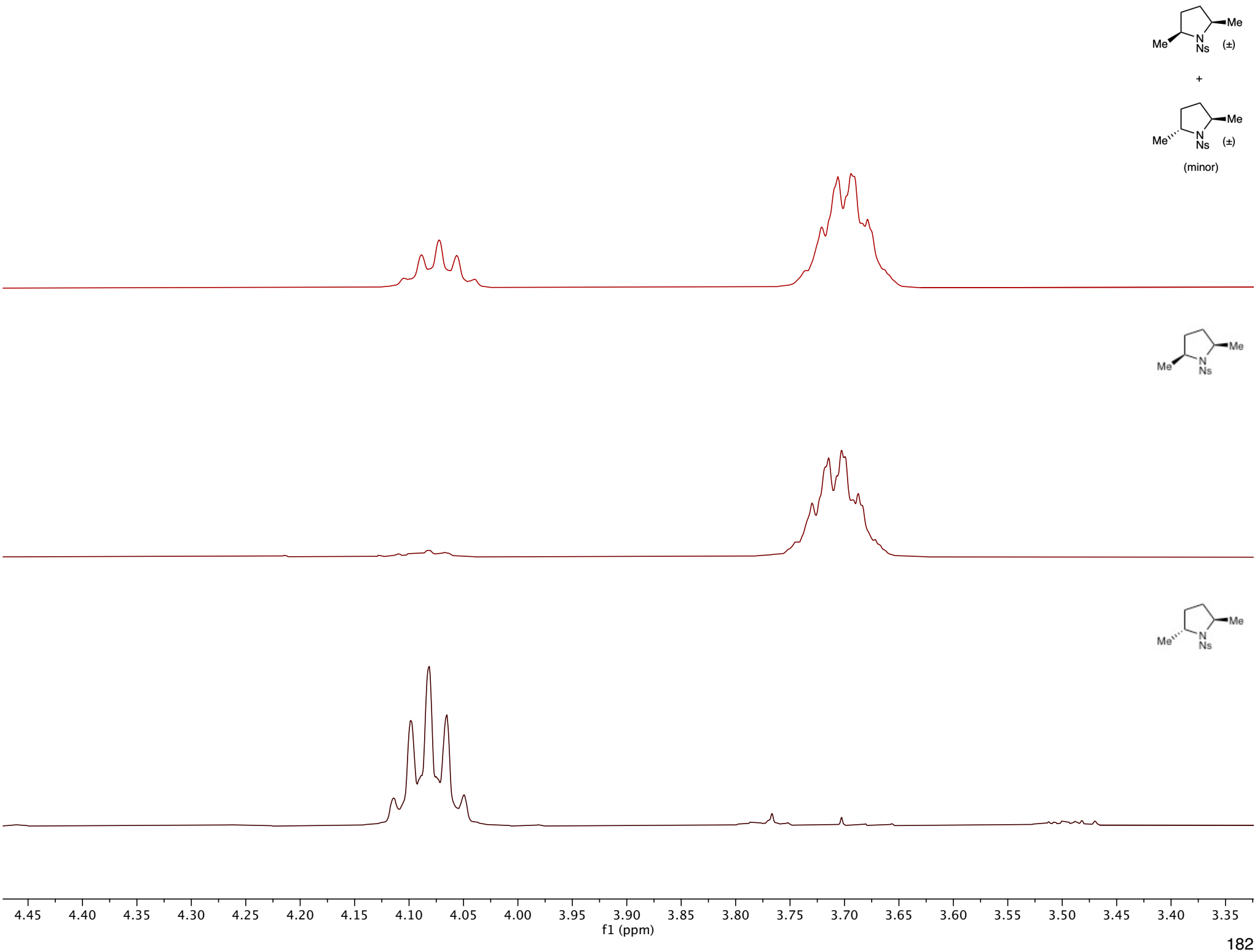


	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	58
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

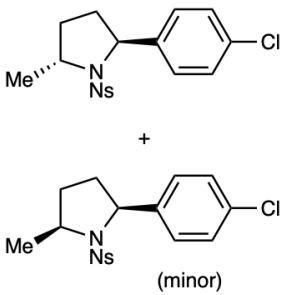


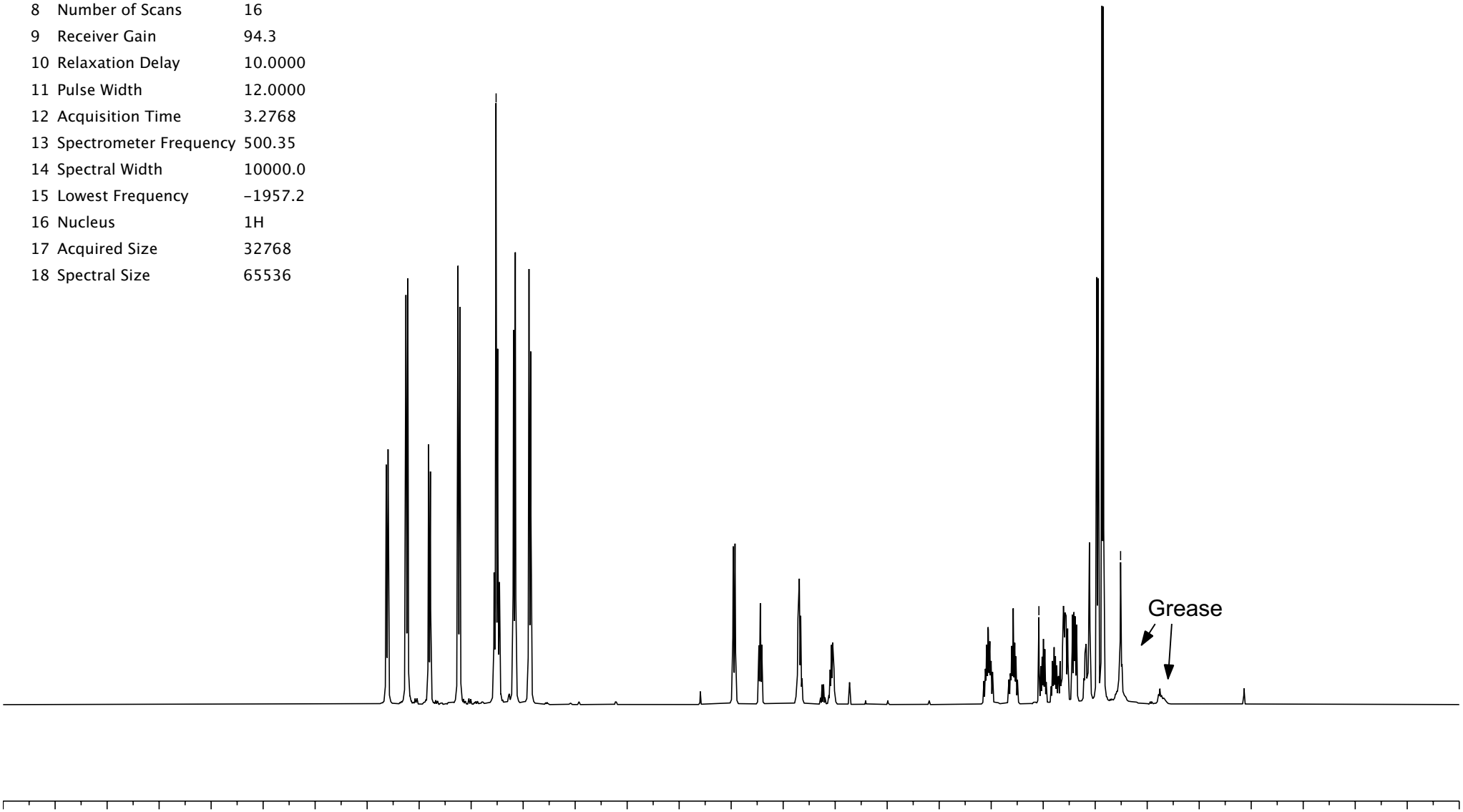
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	46
10	Relaxation Delay	10.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

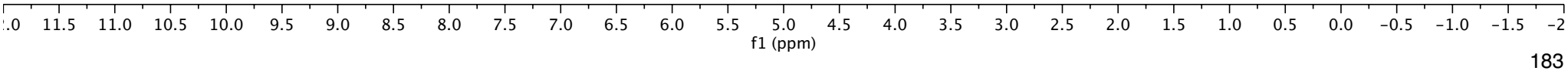



Me
Me
N
Ns
(±)
+
Me
Me
N
Ns
(±)
(minor)
Me
Me
N
Ns
Me
Me
N
Ns
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
3.35
f1 (ppm)

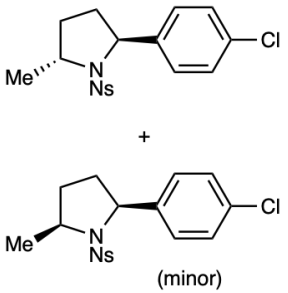
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	94.3
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1957.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536







	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

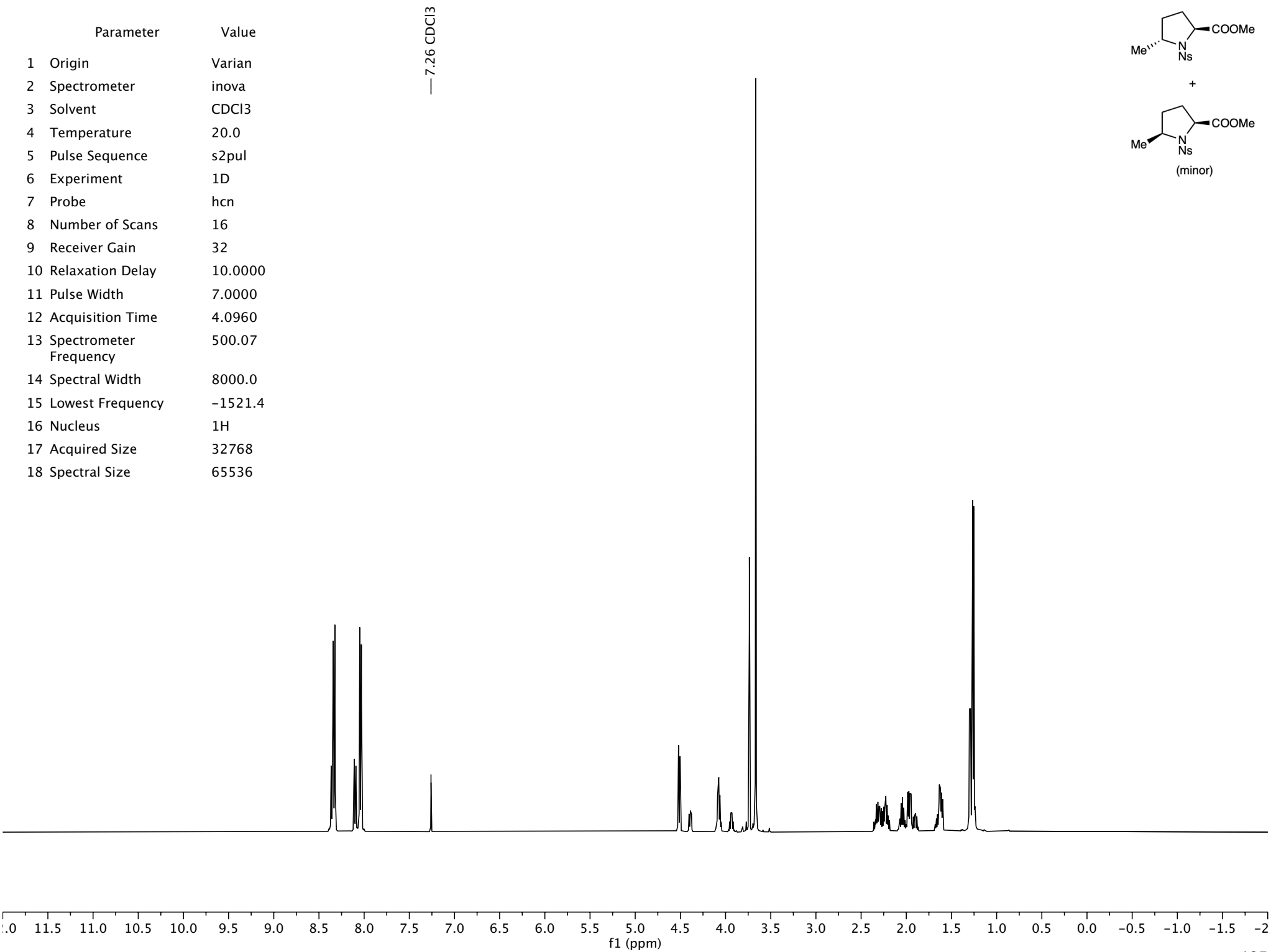


77.16 CDCl3

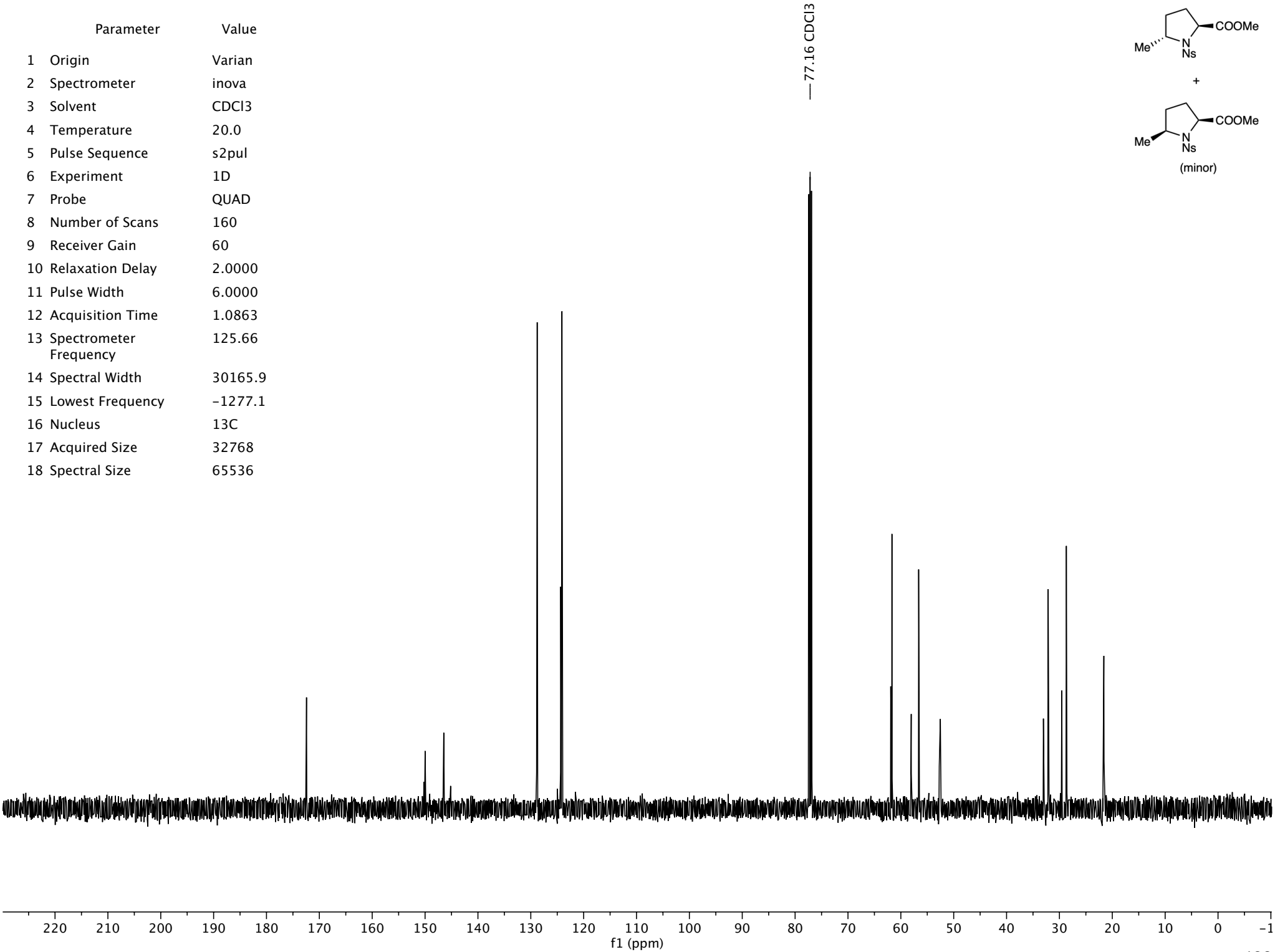
Greas

f1 (ppm)

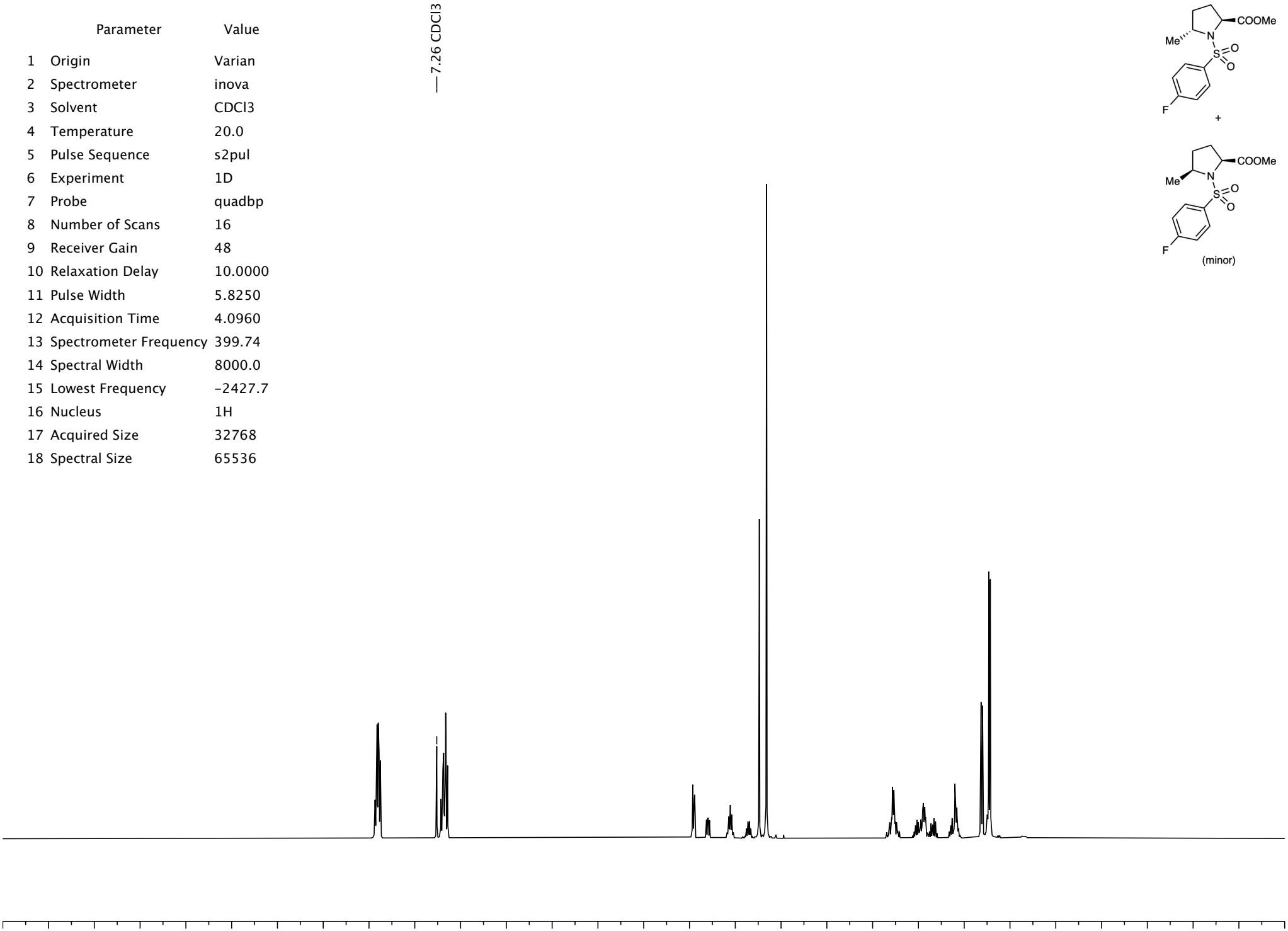
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



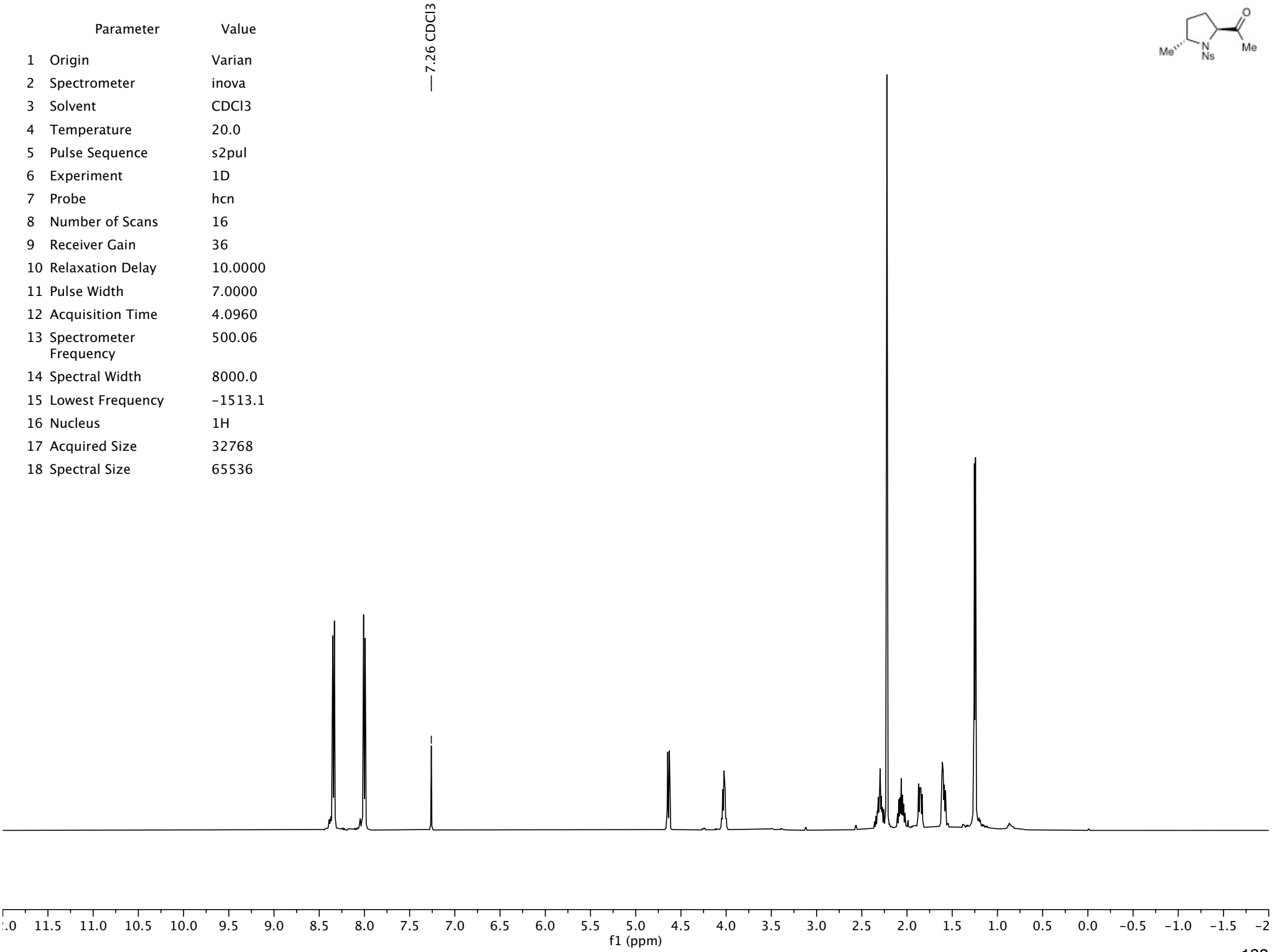
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	160
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	6.0000
12	Acquisition Time	1.0863
13	Spectrometer Frequency	125.66
14	Spectral Width	30165.9
15	Lowest Frequency	-1277.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



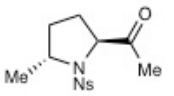
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	10.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

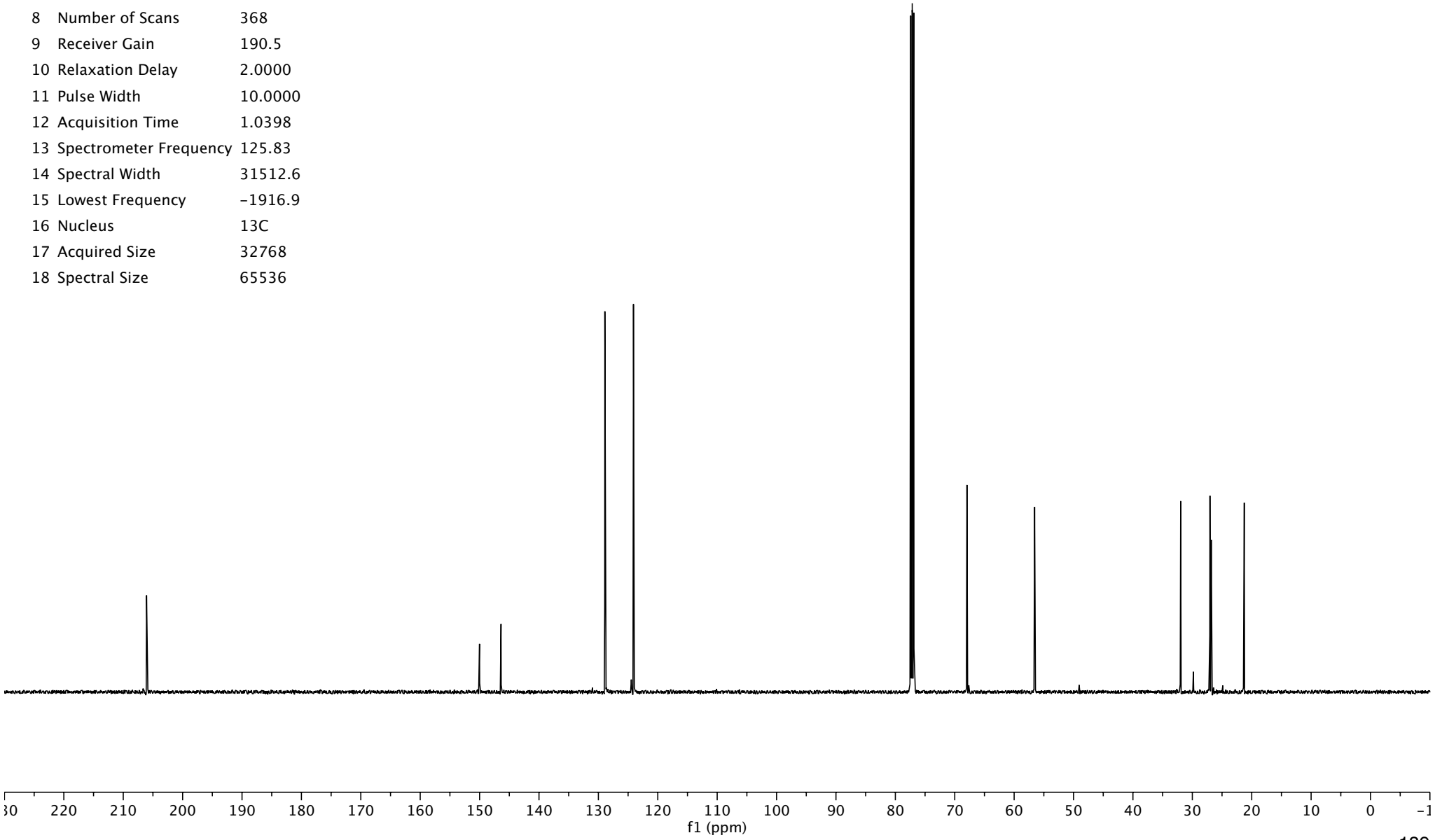


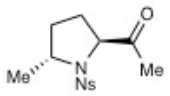
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	36
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



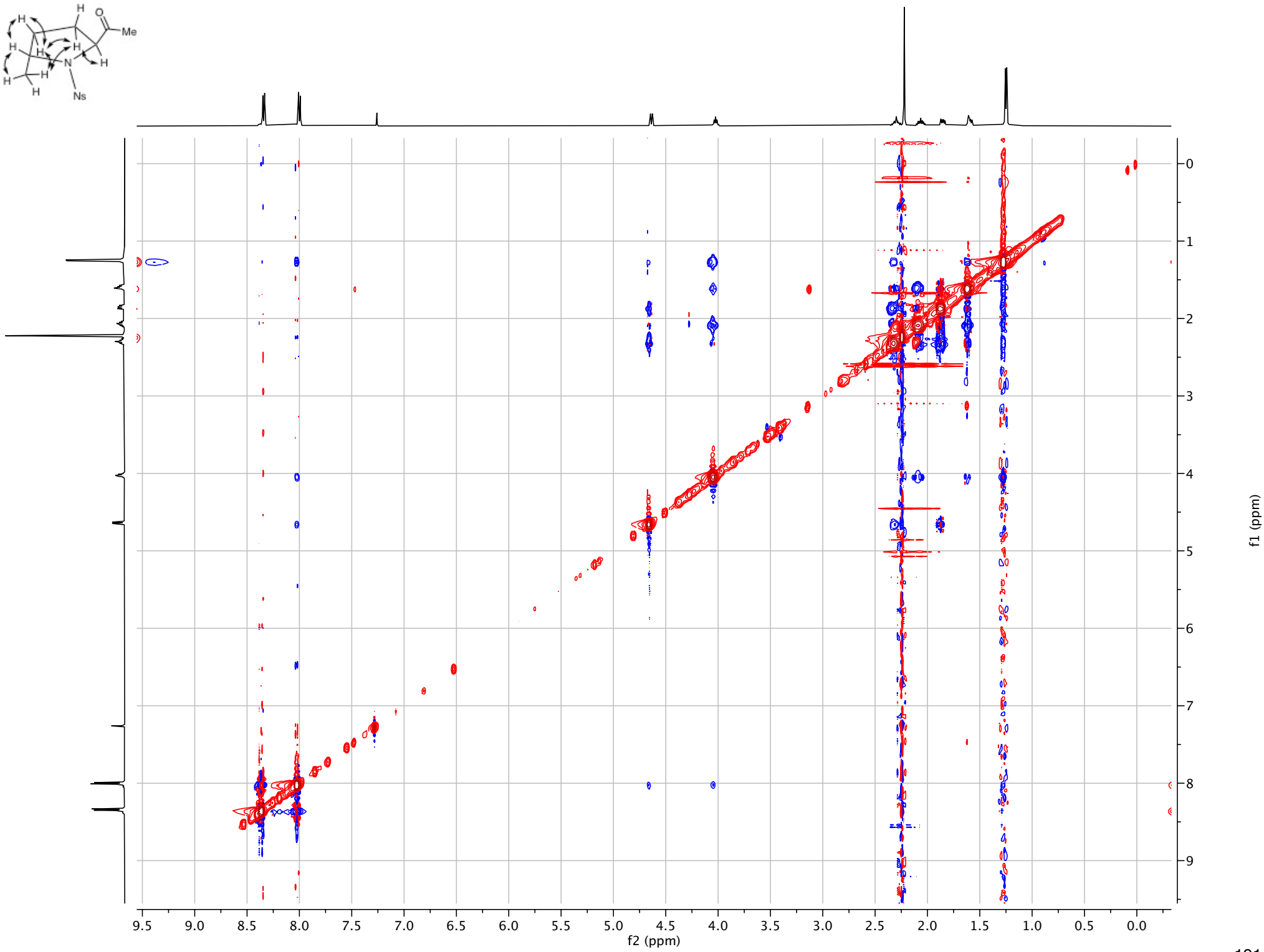
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



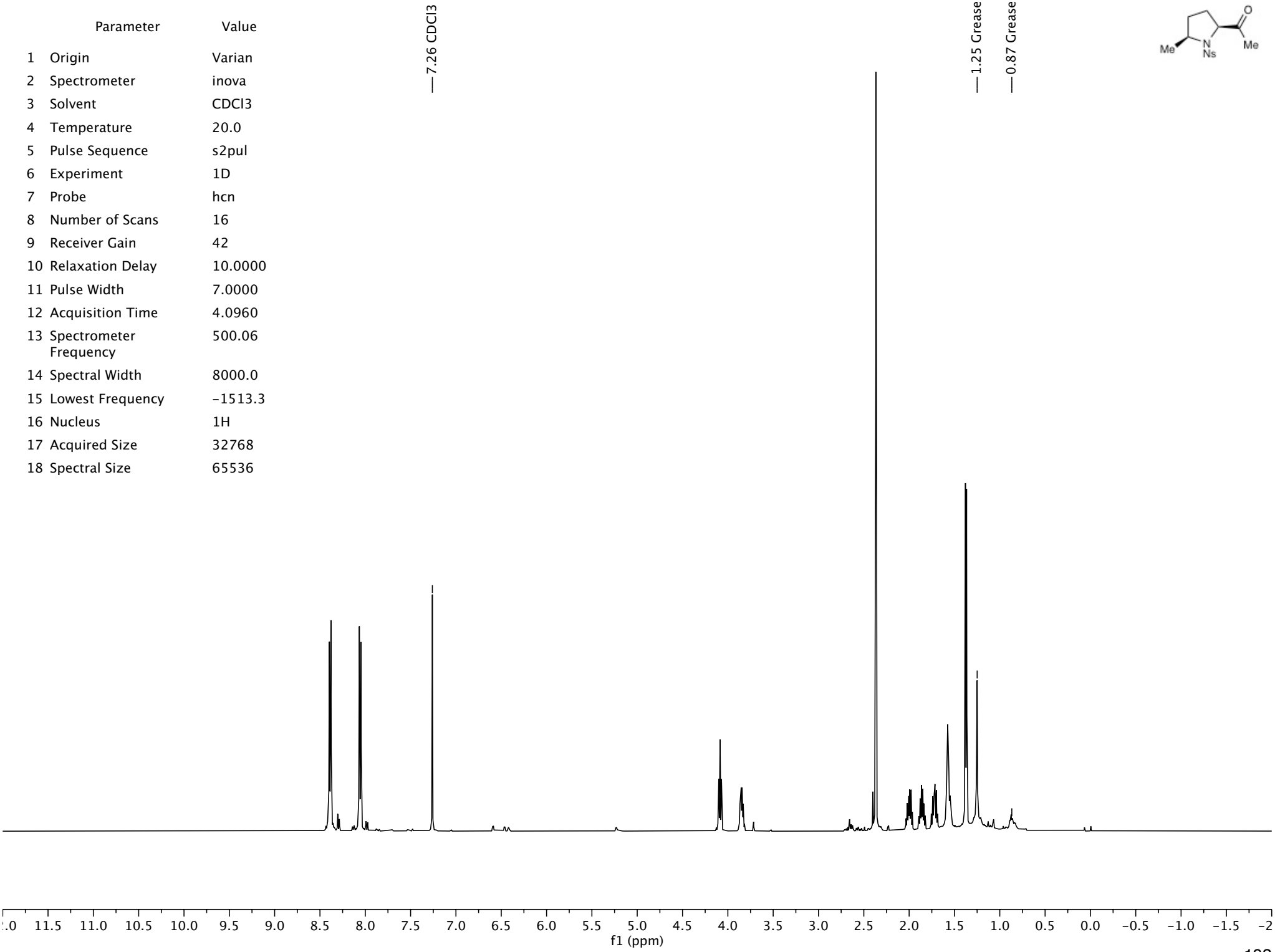




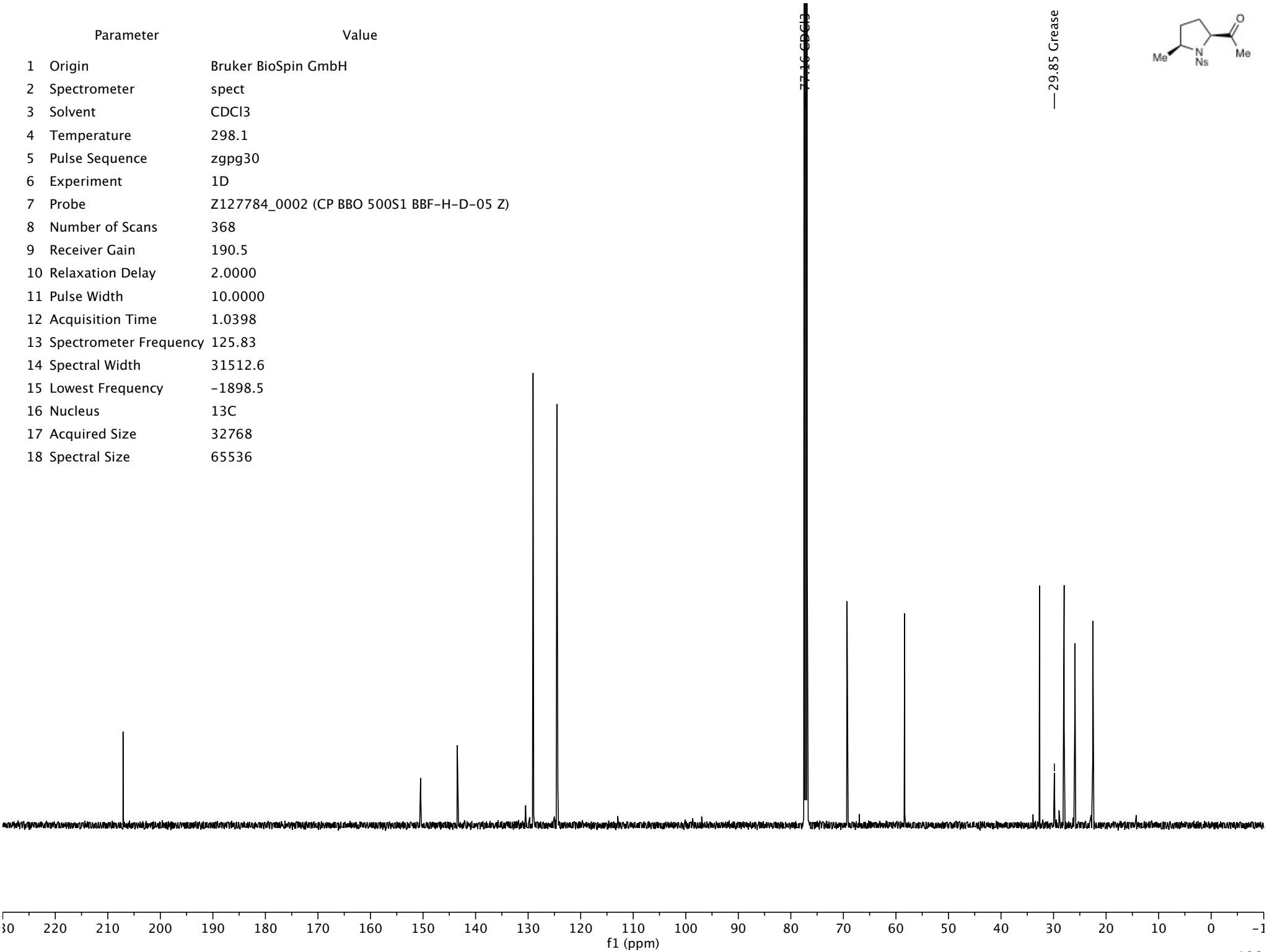
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	cosygpppqf
6	Experiment	COSY
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1
9	Receiver Gain	34.8
10	Relaxation Delay	1.9504
11	Pulse Width	12.0000
12	Acquisition Time	0.2068
13	Spectrometer Frequency	(500.35, 500.35)
14	Spectral Width	(4950.5, 4950.5)
15	Lowest Frequency	(-170.2, -170.2)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)

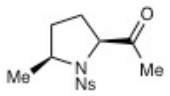

H
O
Me
H
H
H
H
N
H
H
H
H
Ns
f2 (ppm)
f1 (ppm)

	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.3
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

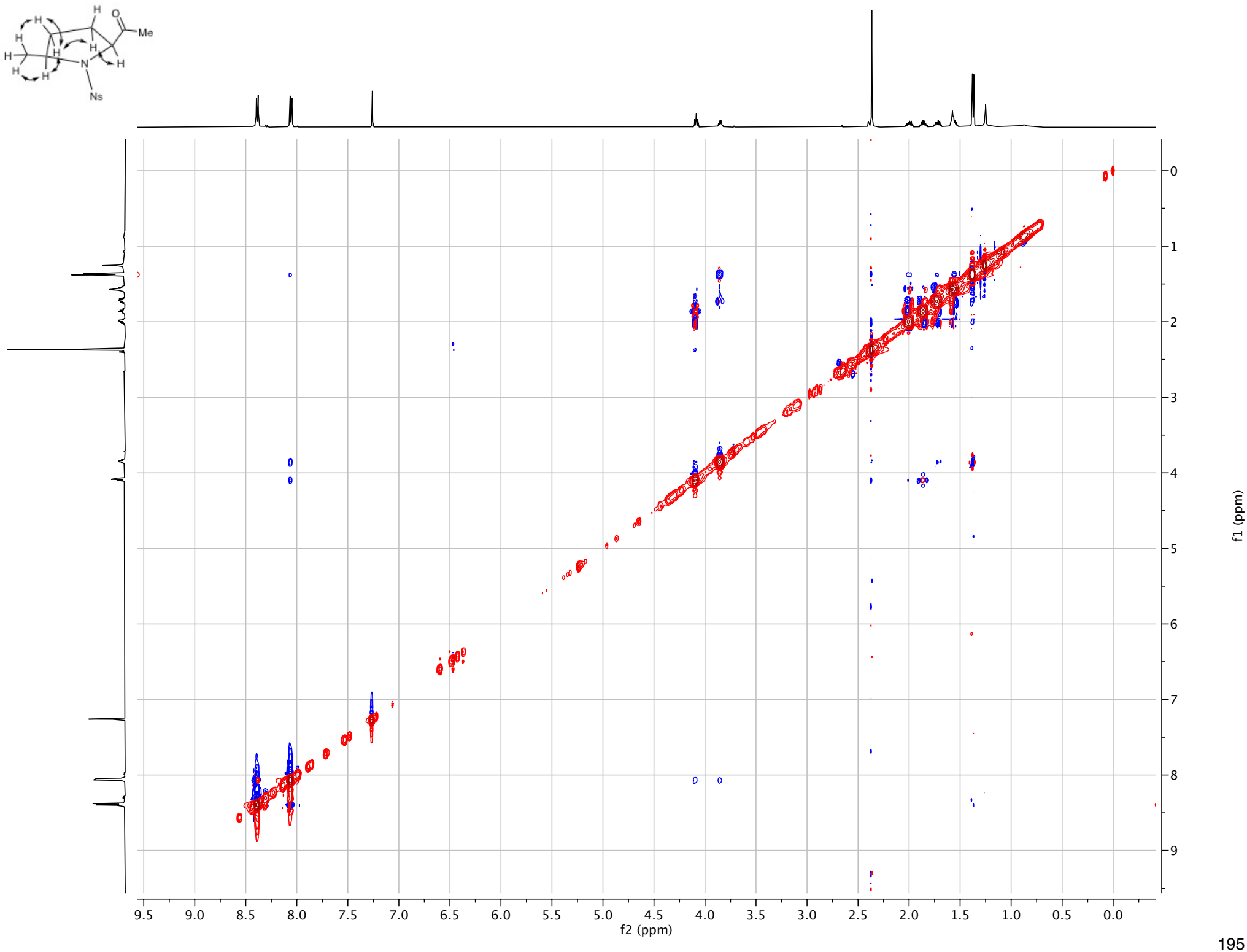


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

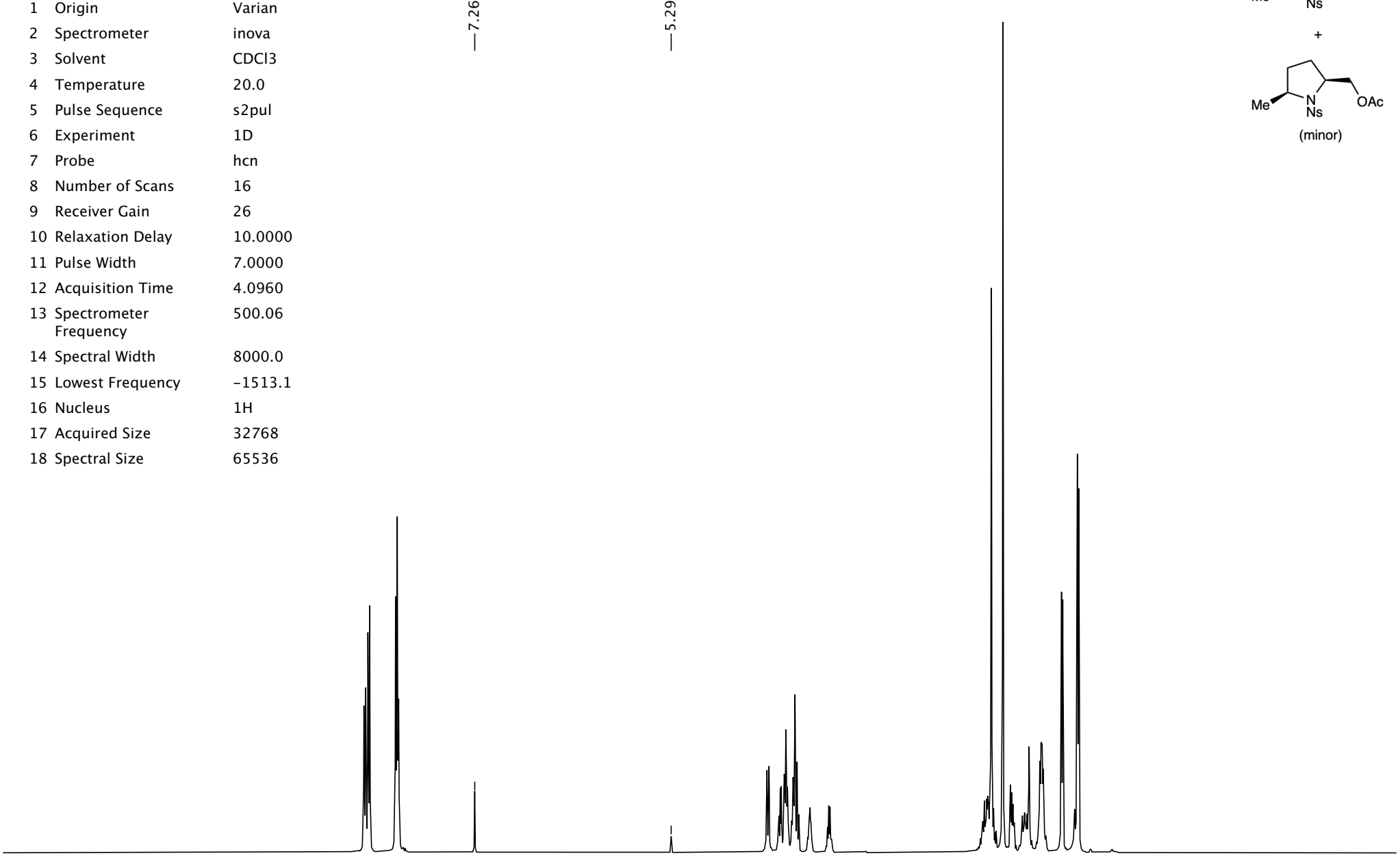




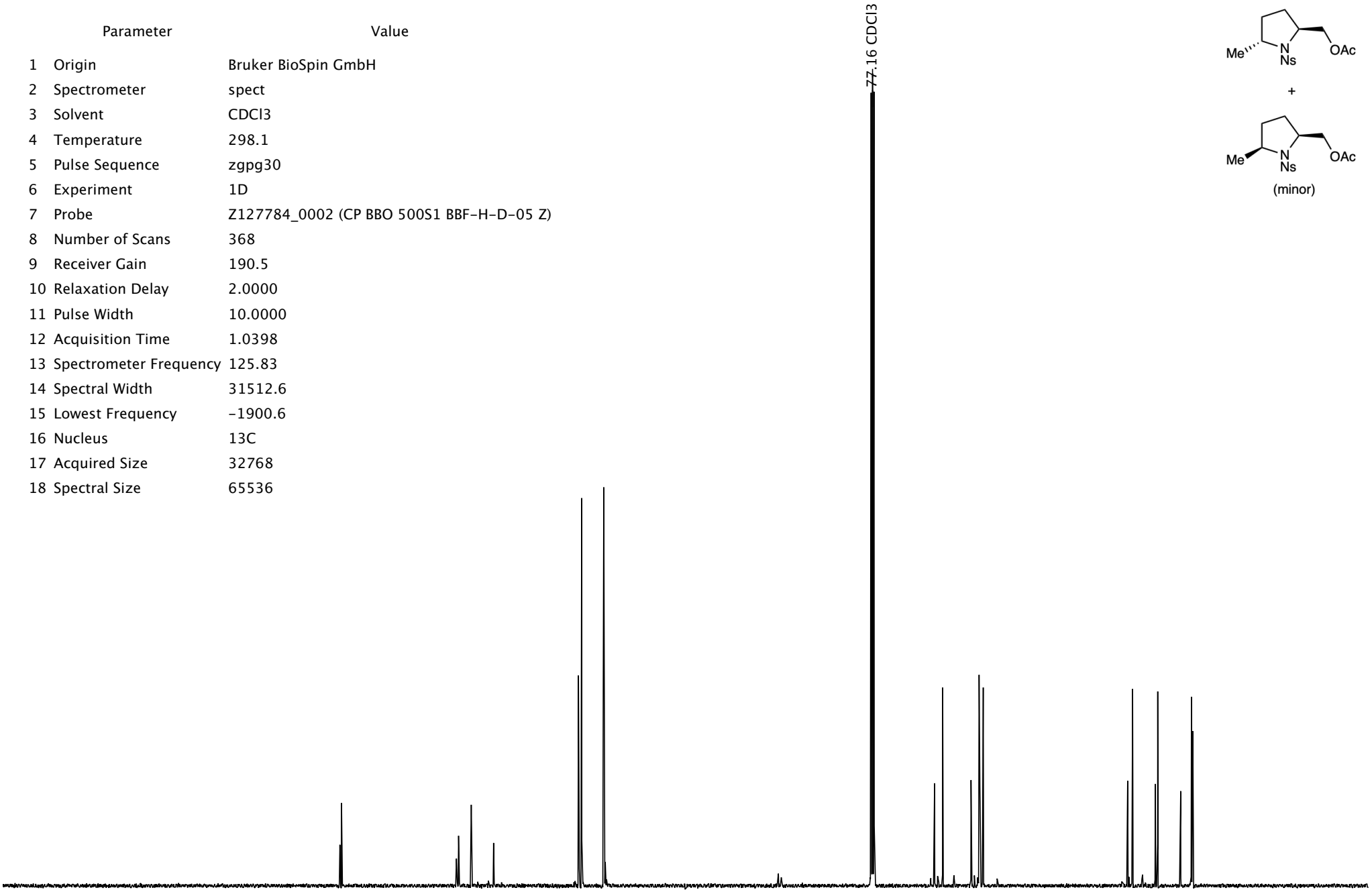
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	cosygpppqf
6	Experiment	COSY
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	4
9	Receiver Gain	61.8
10	Relaxation Delay	1.9525
11	Pulse Width	12.0000
12	Acquisition Time	0.2048
13	Spectrometer Frequency	(500.35, 500.35)
14	Spectral Width	(5000.0, 5000.0)
15	Lowest Frequency	(-214.0, -214.0)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)


Me
Ns
f2 (ppm)
f1 (ppm)

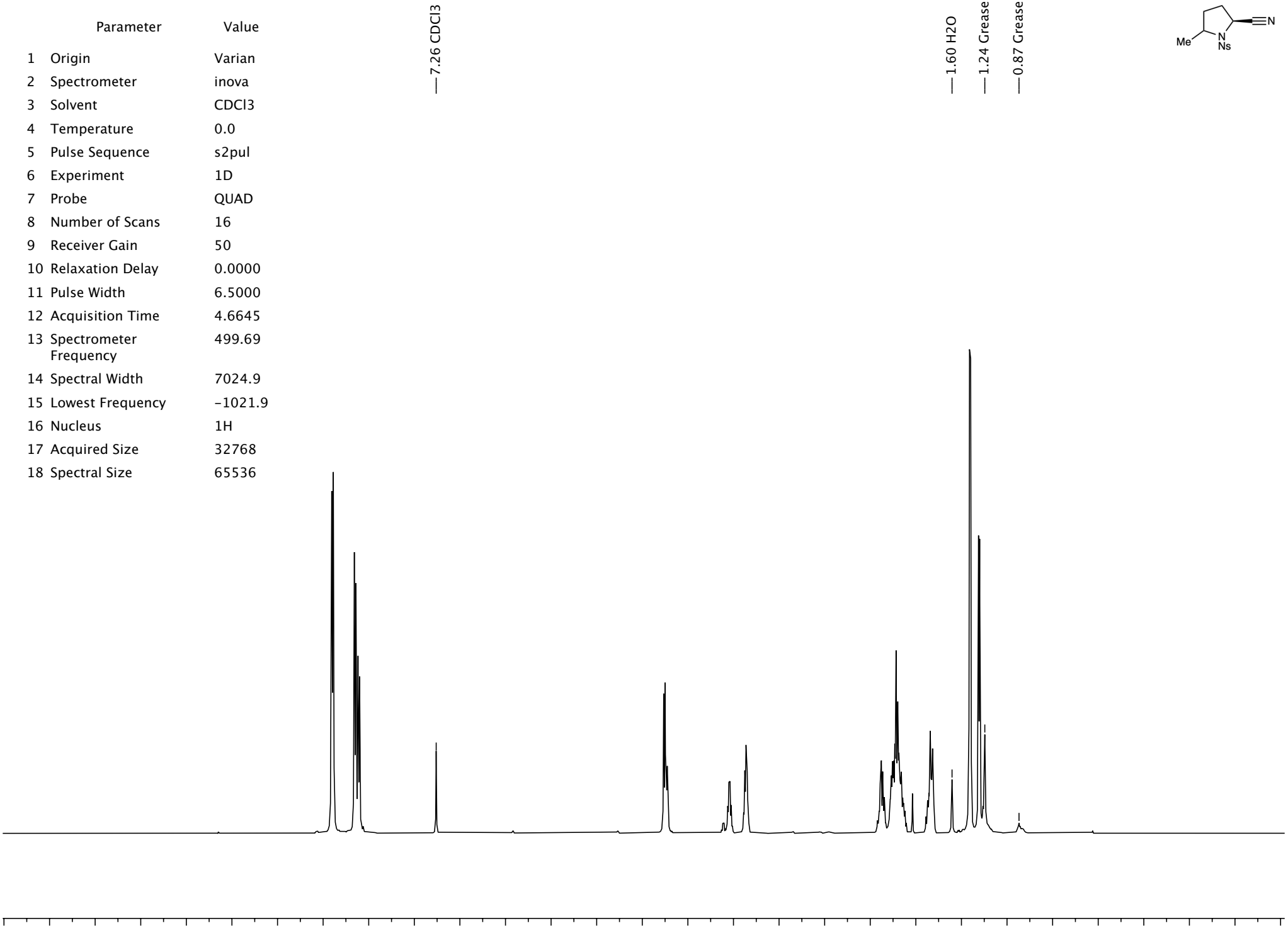
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	26
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



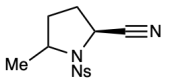
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



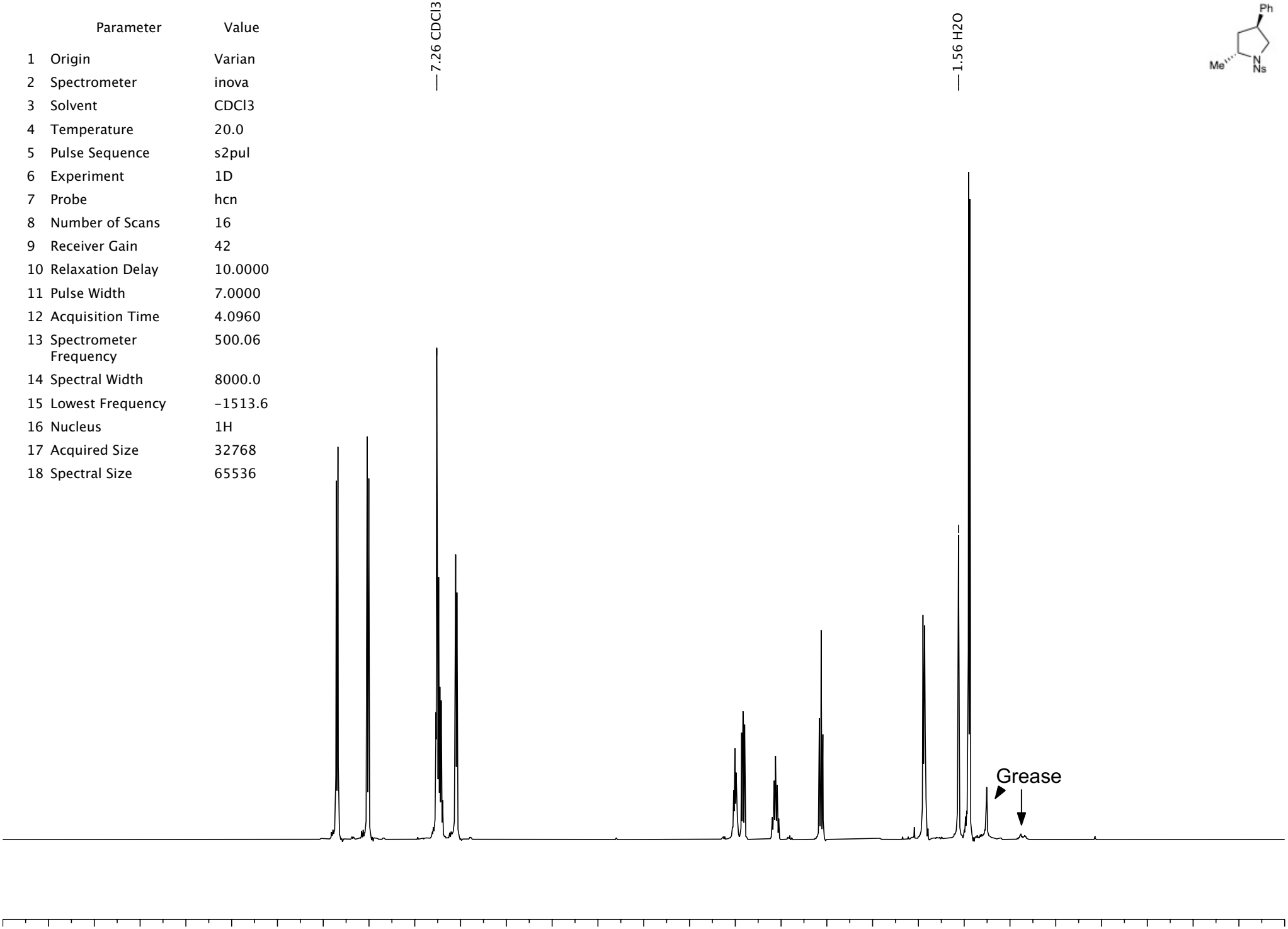
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	0.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	50
10	Relaxation Delay	0.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1021.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



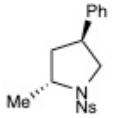
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	0.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	208
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	6.0000
12	Acquisition Time	1.0863
13	Spectrometer Frequency	125.66
14	Spectral Width	30165.9
15	Lowest Frequency	-1260.2
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



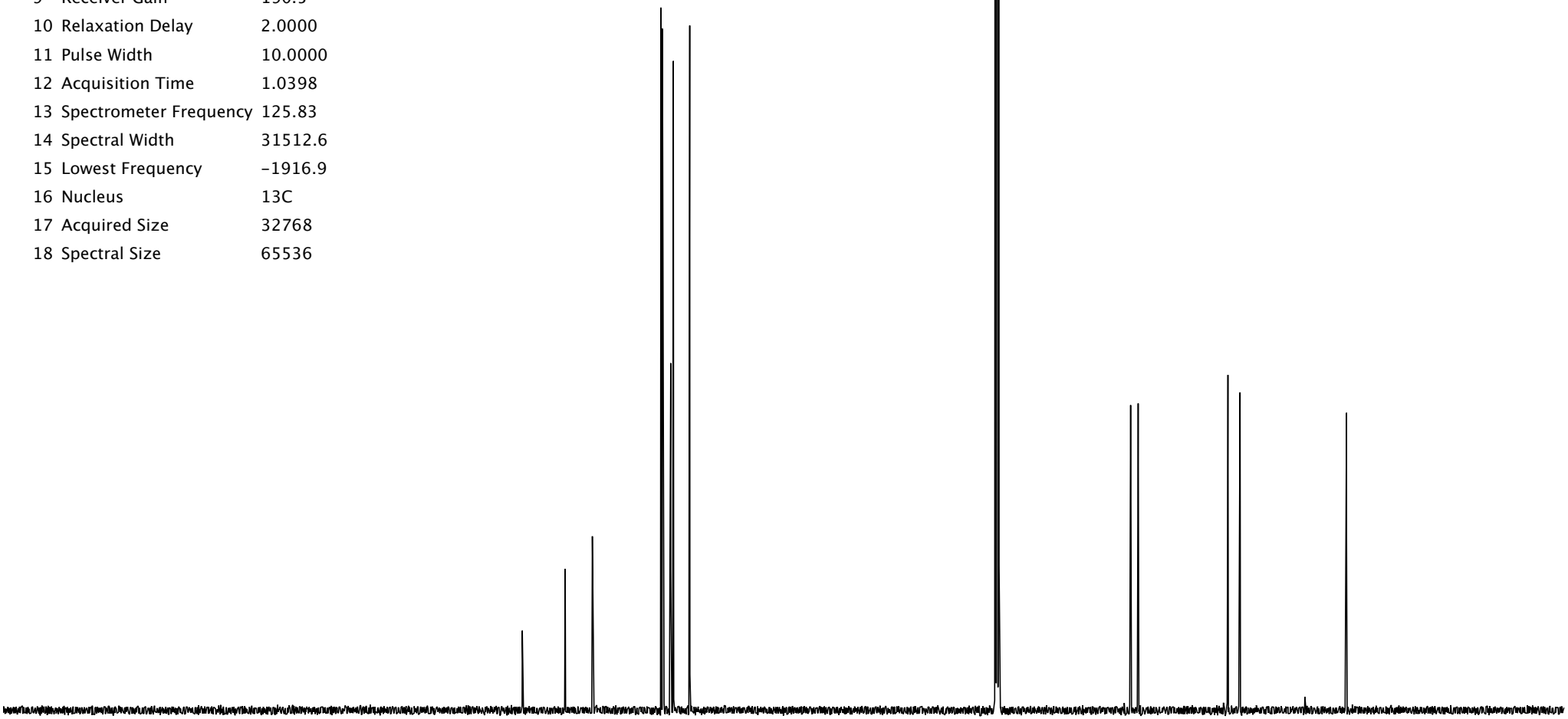
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.6
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

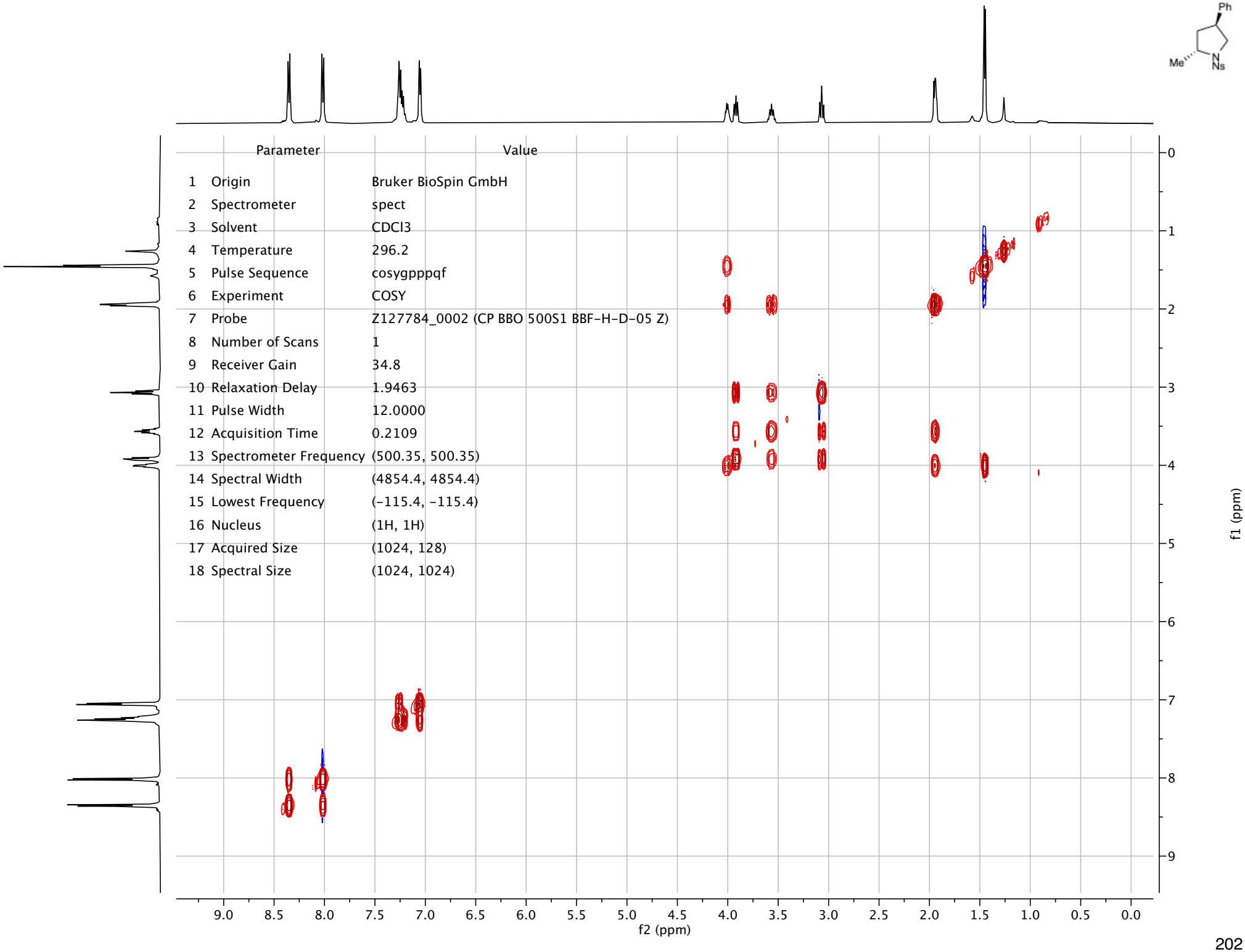


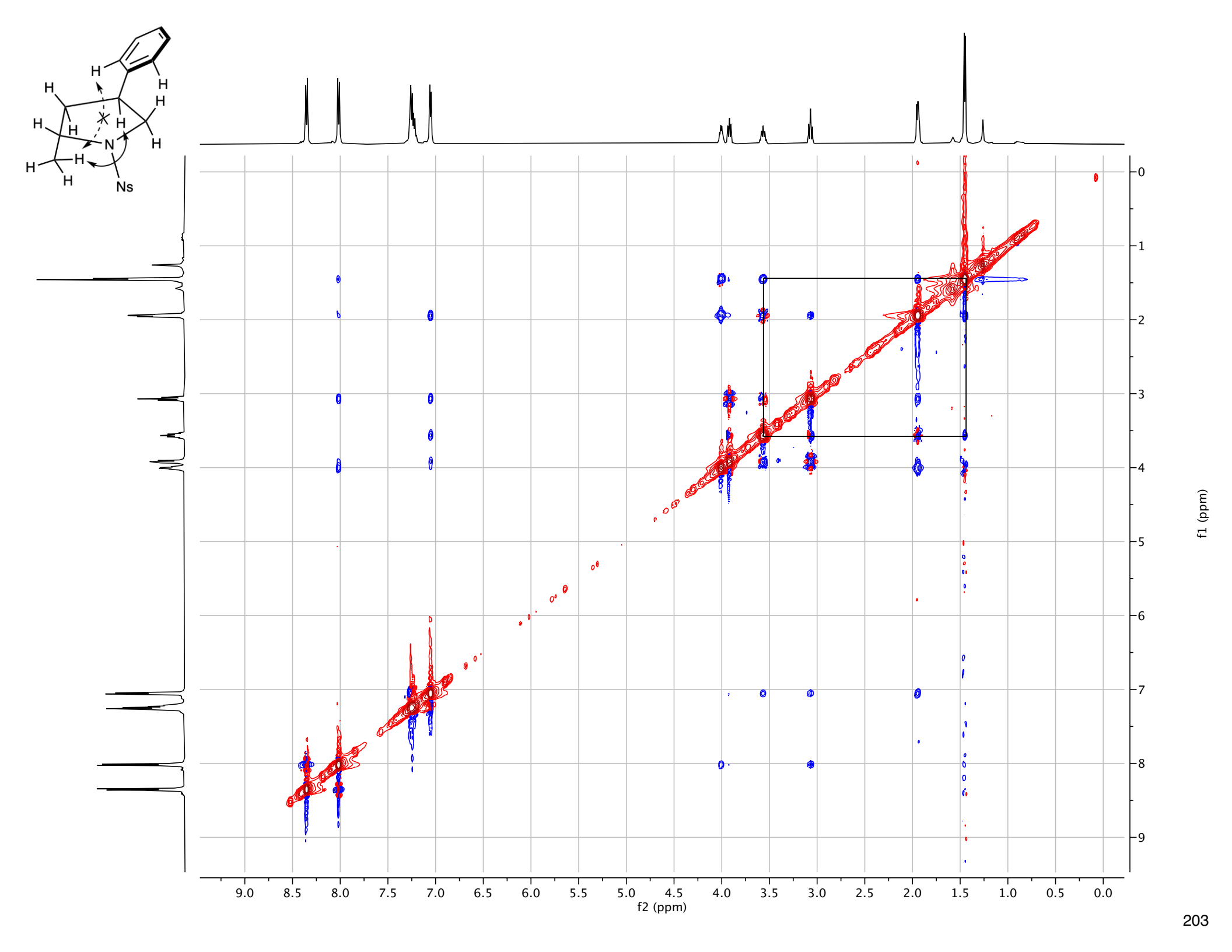
77.16 CDCl3



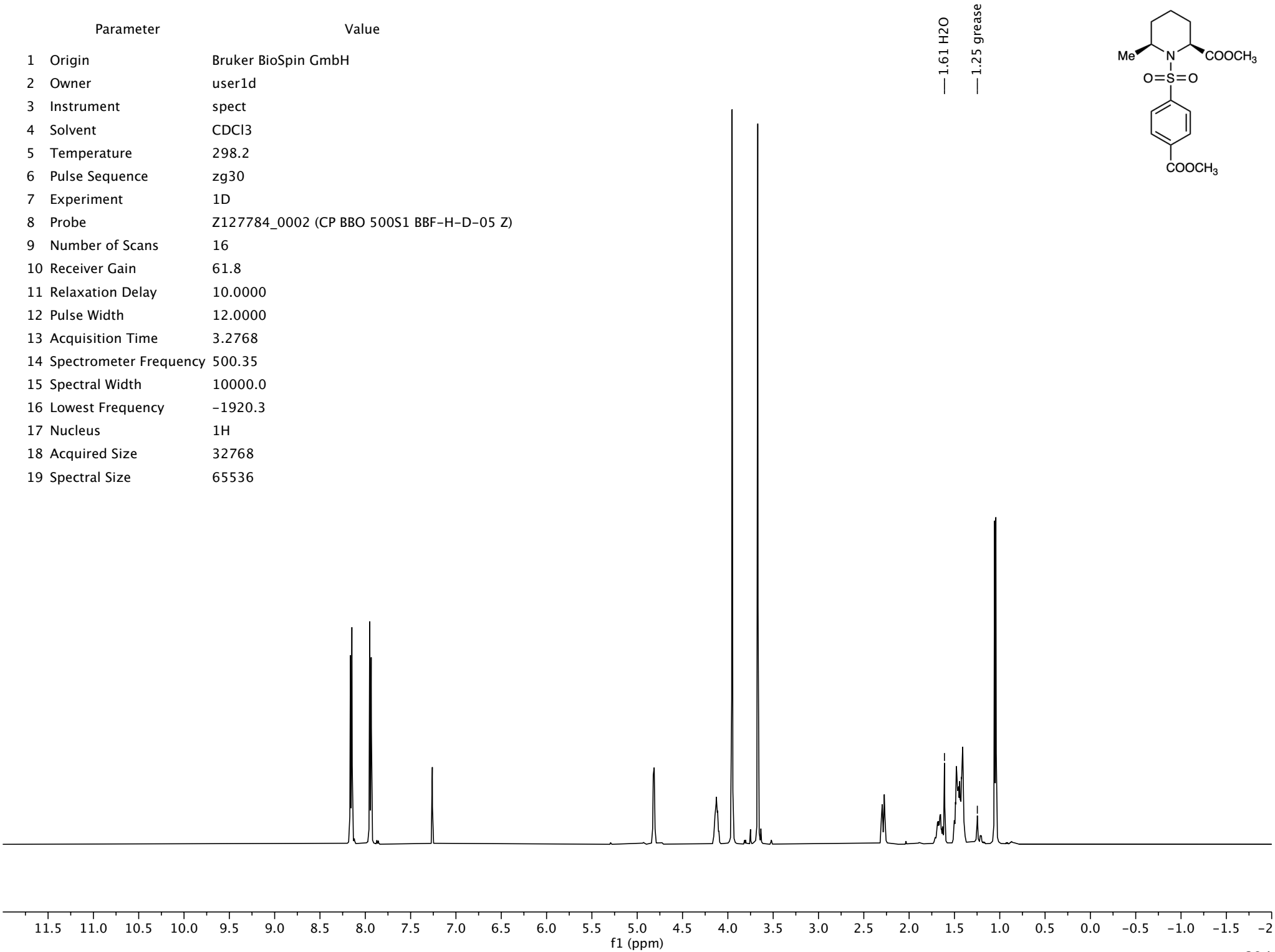
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

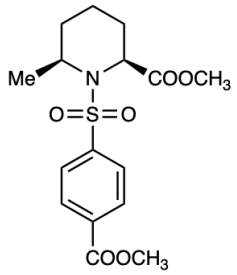

Ph
Me
N
Ns
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 296.2
5 Pulse Sequence cosygpppqf
6 Experiment COSY
7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans 1
9 Receiver Gain 34.8
10 Relaxation Delay 1.9463
11 Pulse Width 12.0000
12 Acquisition Time 0.2109
13 Spectrometer Frequency (500.35, 500.35)
14 Spectral Width (4854.4, 4854.4)
15 Lowest Frequency (-115.4, -115.4)
16 Nucleus (1H, 1H)
17 Acquired Size (1024, 128)
18 Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)

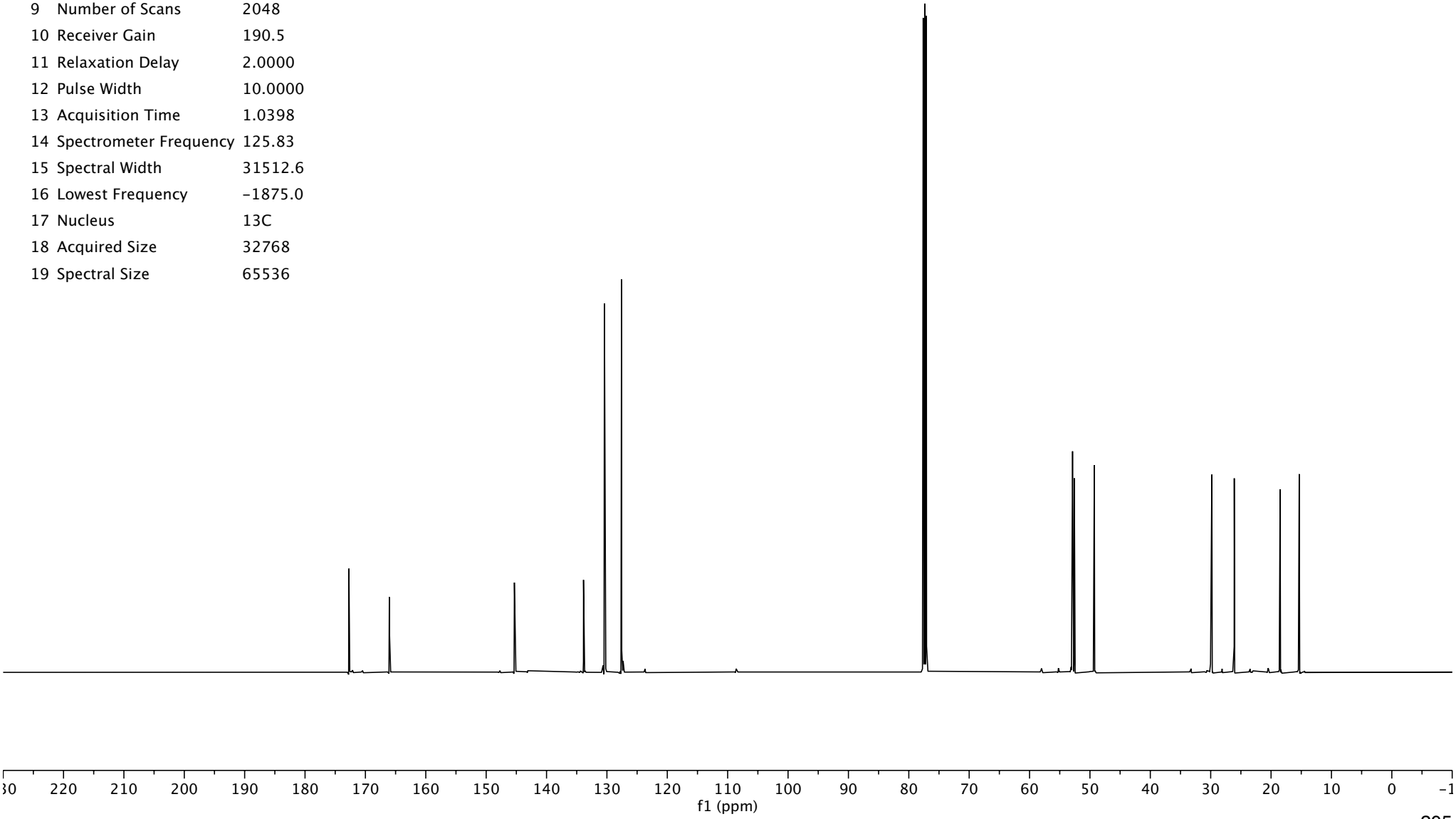

H
H
H
H
H
H
H
H
H
H
N
Ns
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

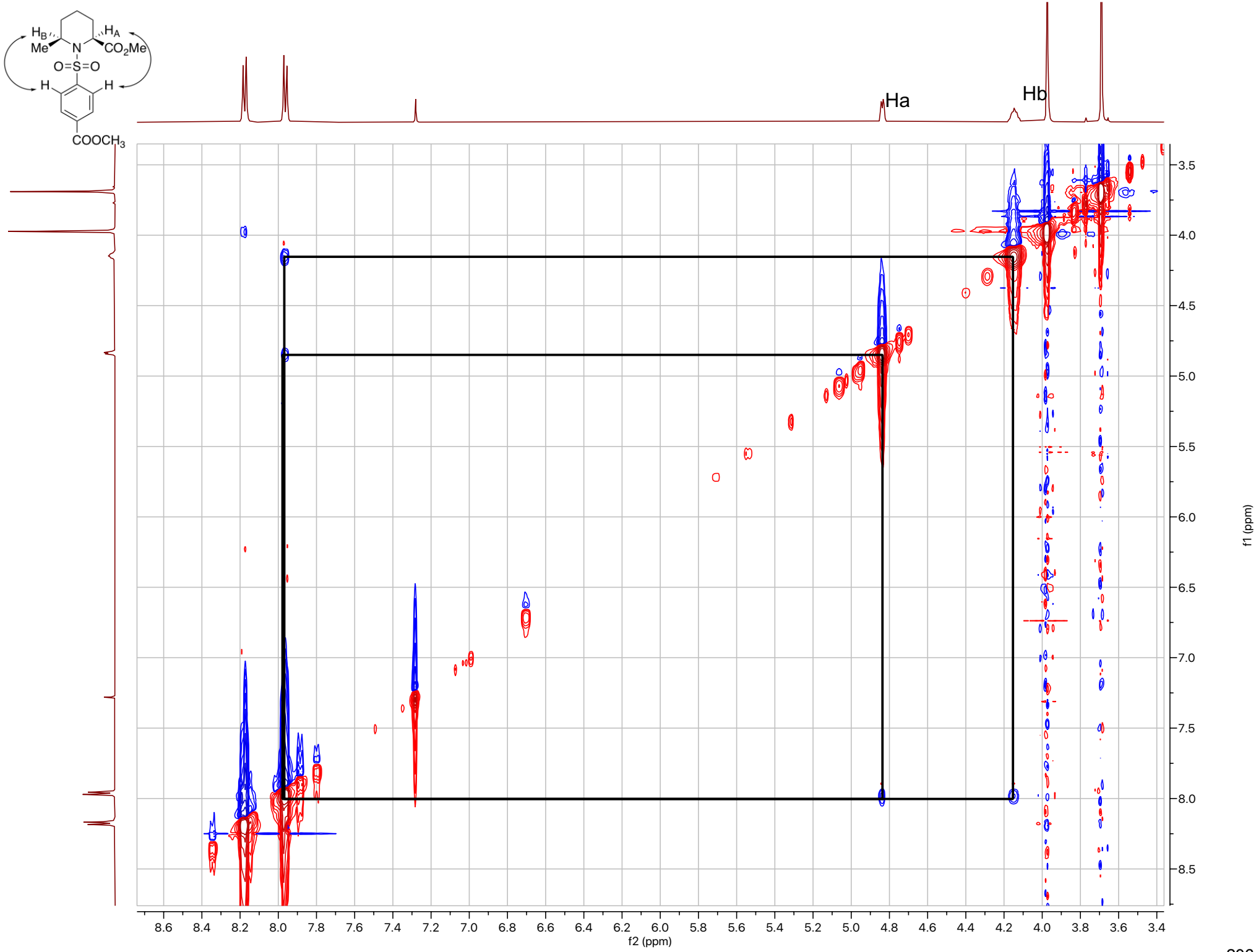
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	61.8
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

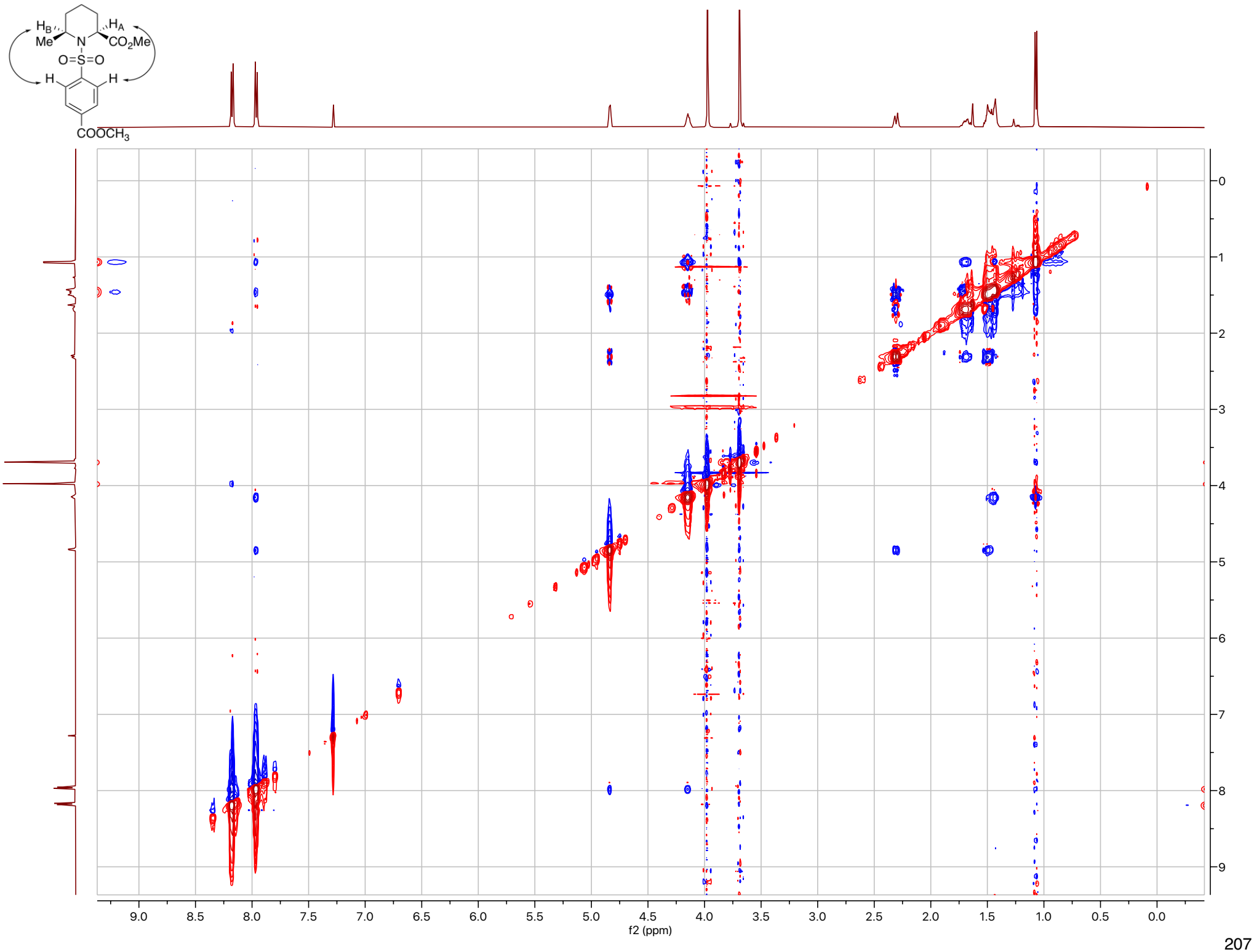


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1875.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



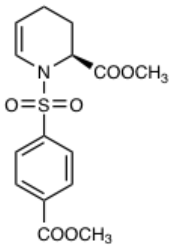


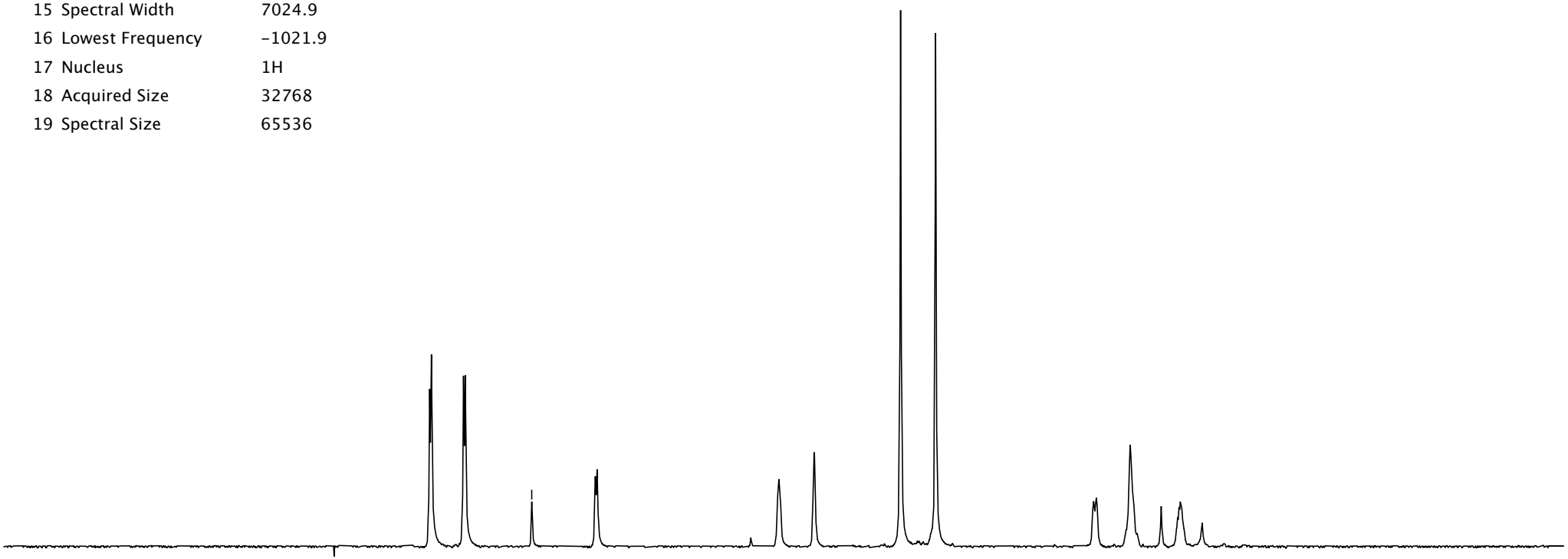

Ha
Hb
f2 (ppm)
f1 (ppm)


HB
HA
Me
N
CO2Me
O=S=O
H
H
COOCH3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	60
11	Relaxation Delay	6.0000
12	Pulse Width	6.5000
13	Acquisition Time	4.6645
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

— 7.26 CDCl3

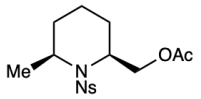


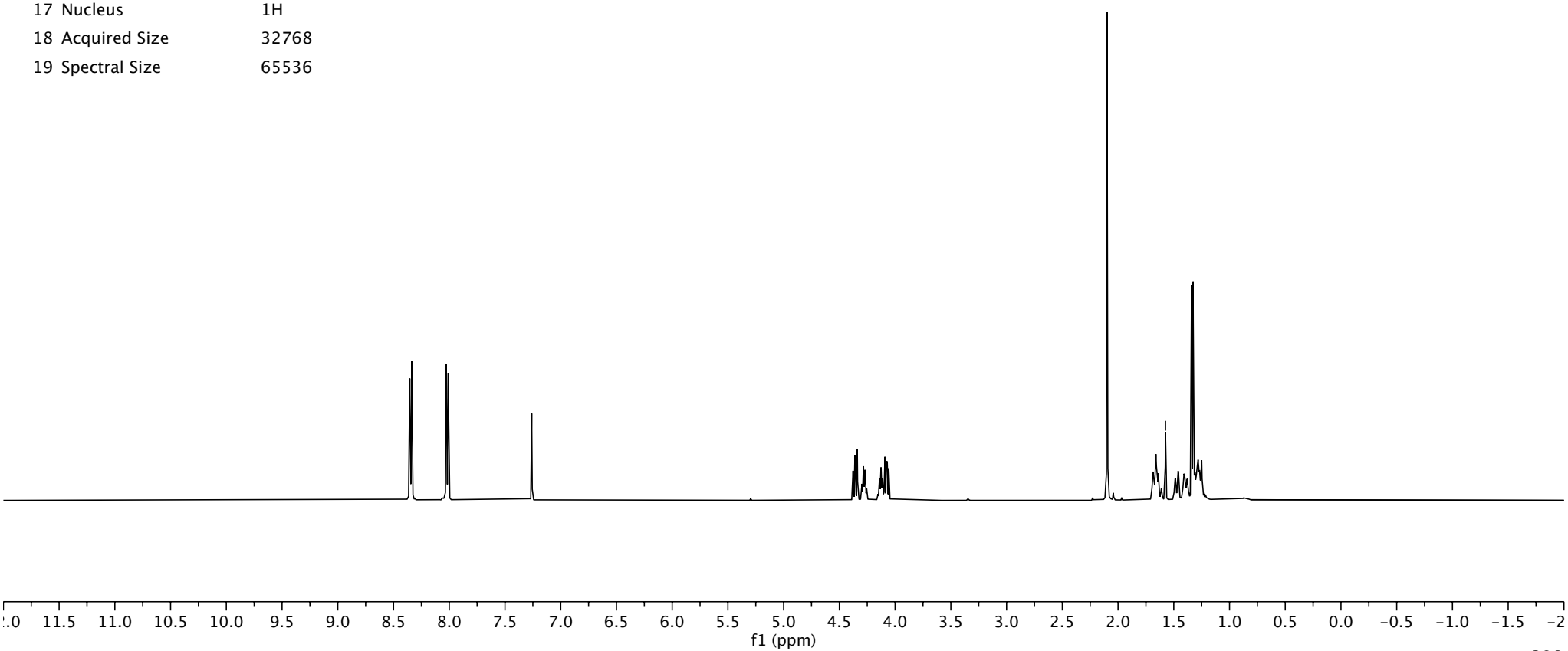


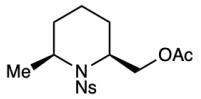
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2

f1 (ppm)

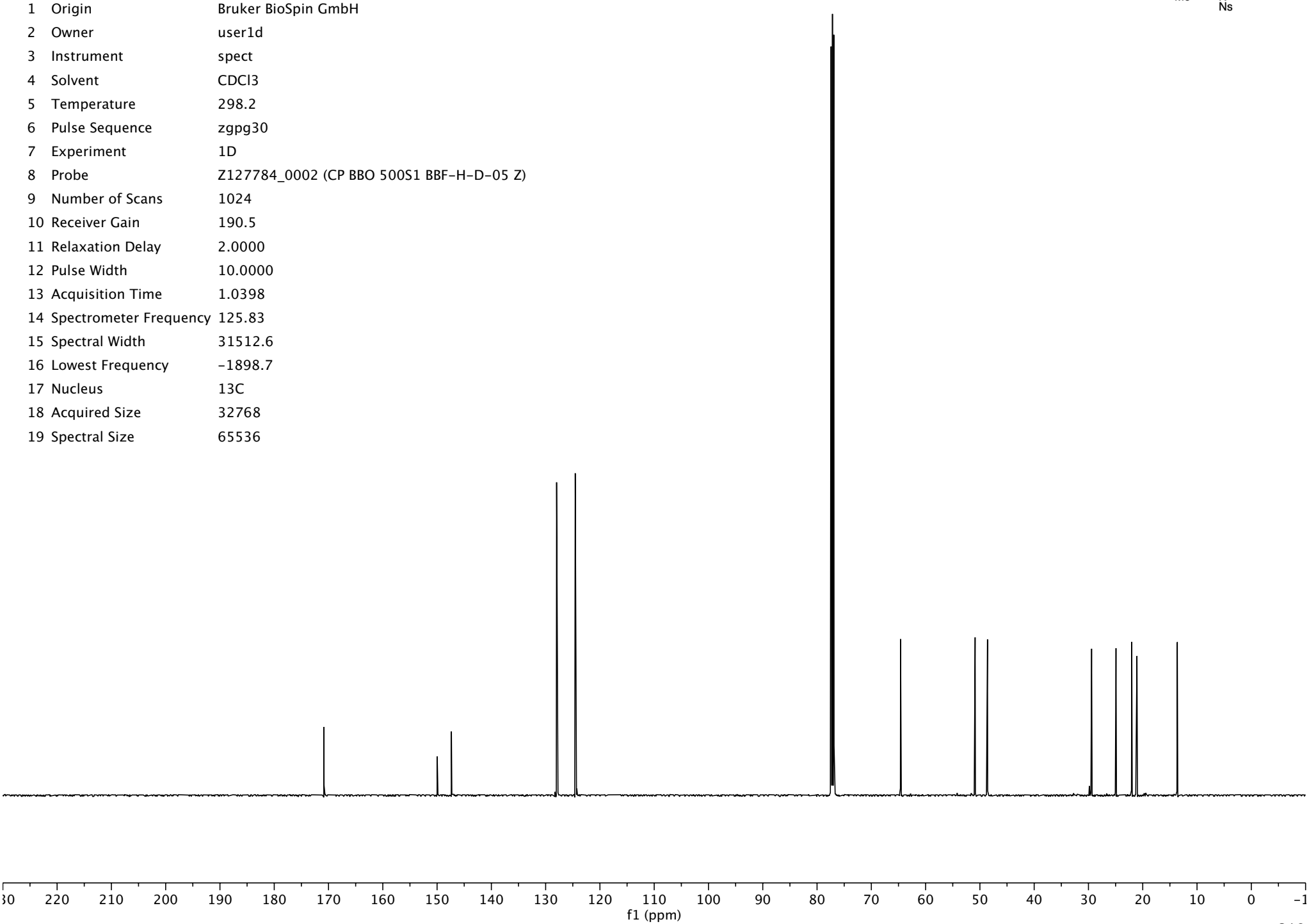
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	94.3
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

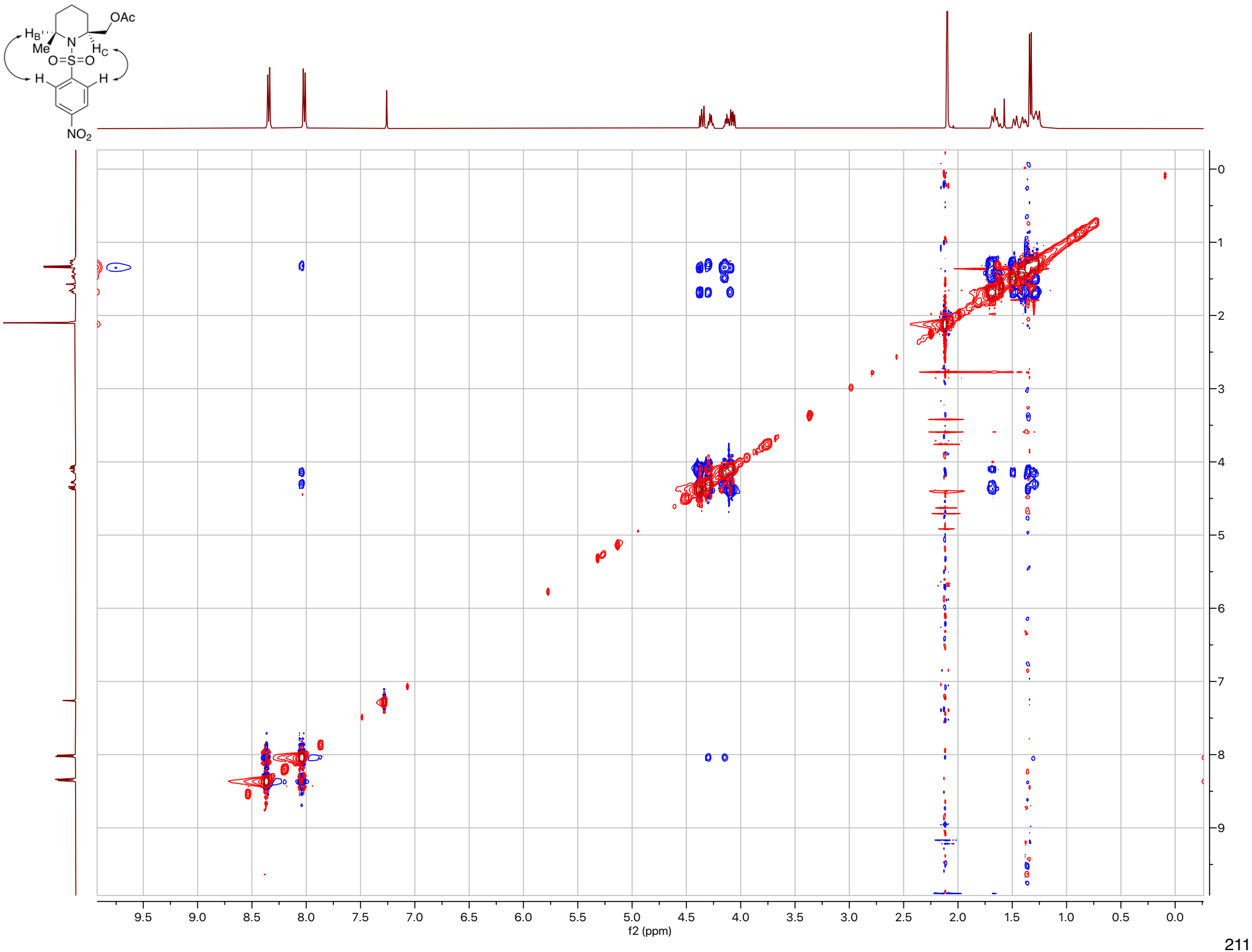


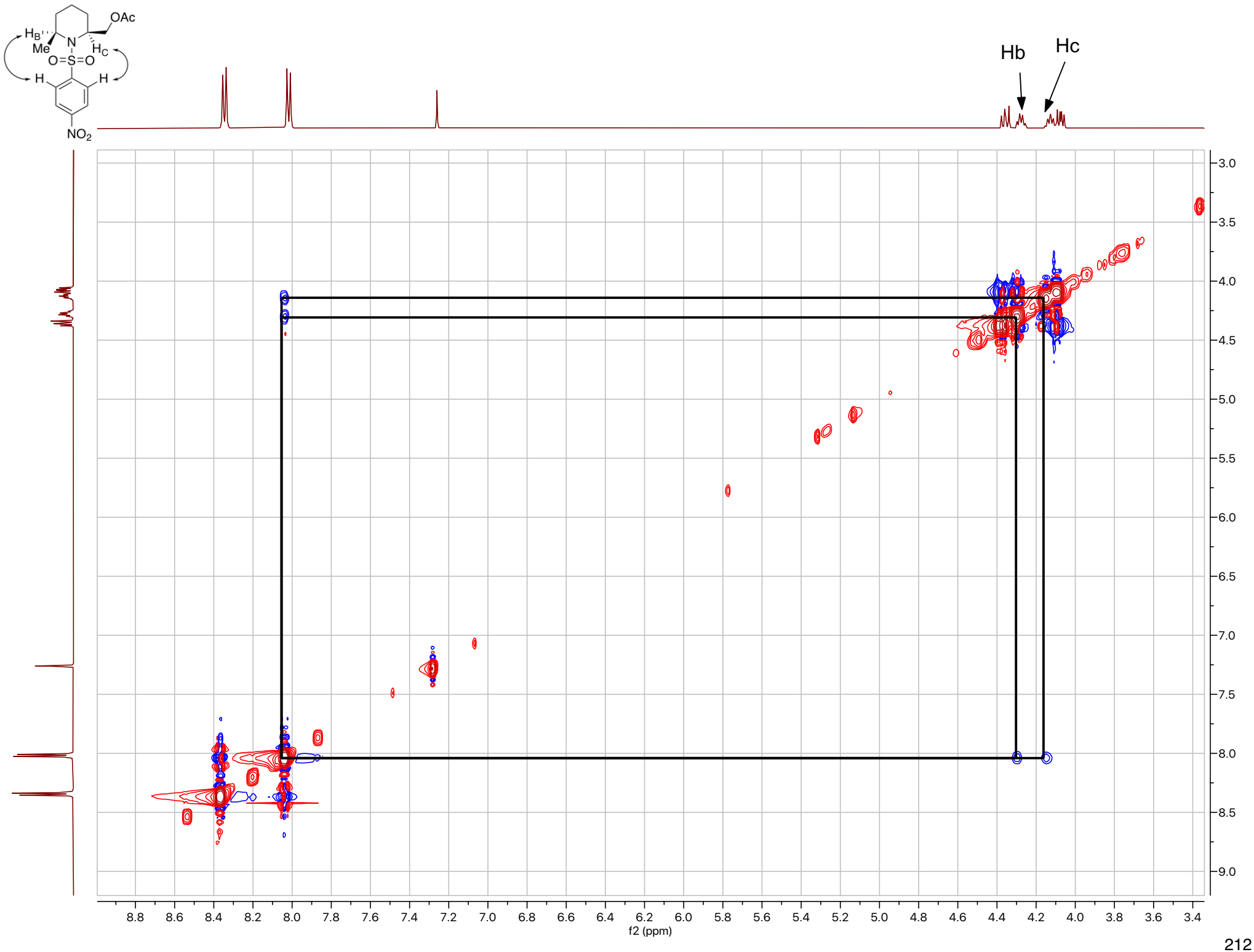




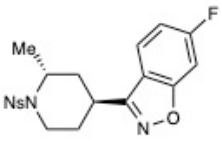
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1898.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536




OAc
H_B
Me
N
H_C
O=S=O
H
H
NO_2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9


OAc
H_B
Me
N
H_C
O=S=O
H
H
NO_2
Hb
Hc
f2 (ppm)

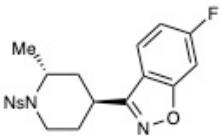
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.3
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1280
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

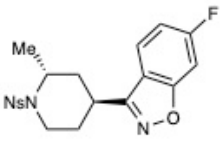
77.16 CDCl3

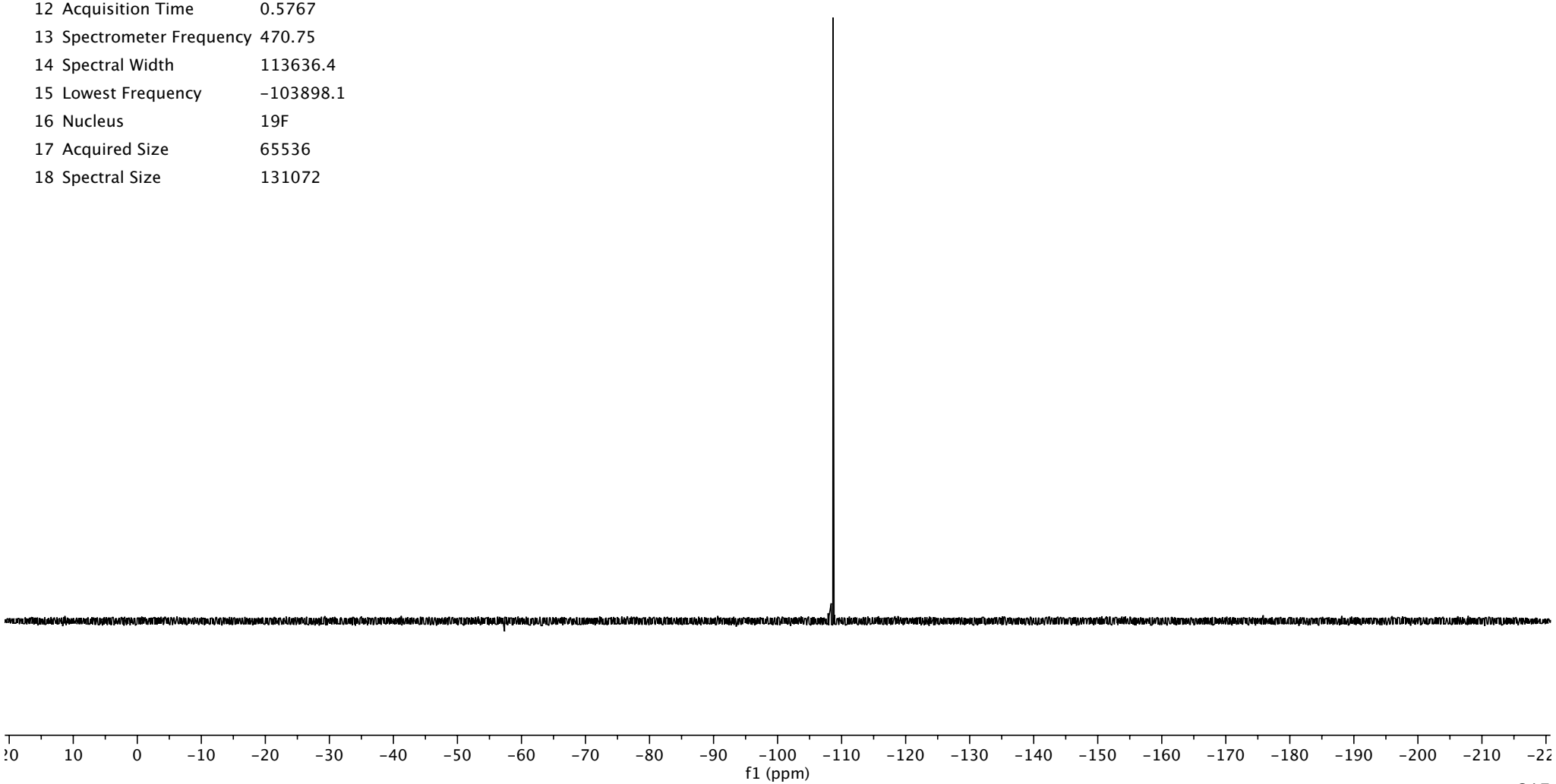
29.85 Grease



f1 (ppm)

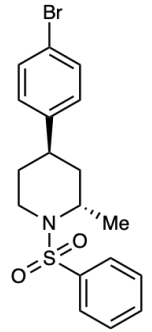
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	15.0000
12	Acquisition Time	0.5767
13	Spectrometer Frequency	470.75
14	Spectral Width	113636.4
15	Lowest Frequency	-103898.1
16	Nucleus	19F
17	Acquired Size	65536
18	Spectral Size	131072

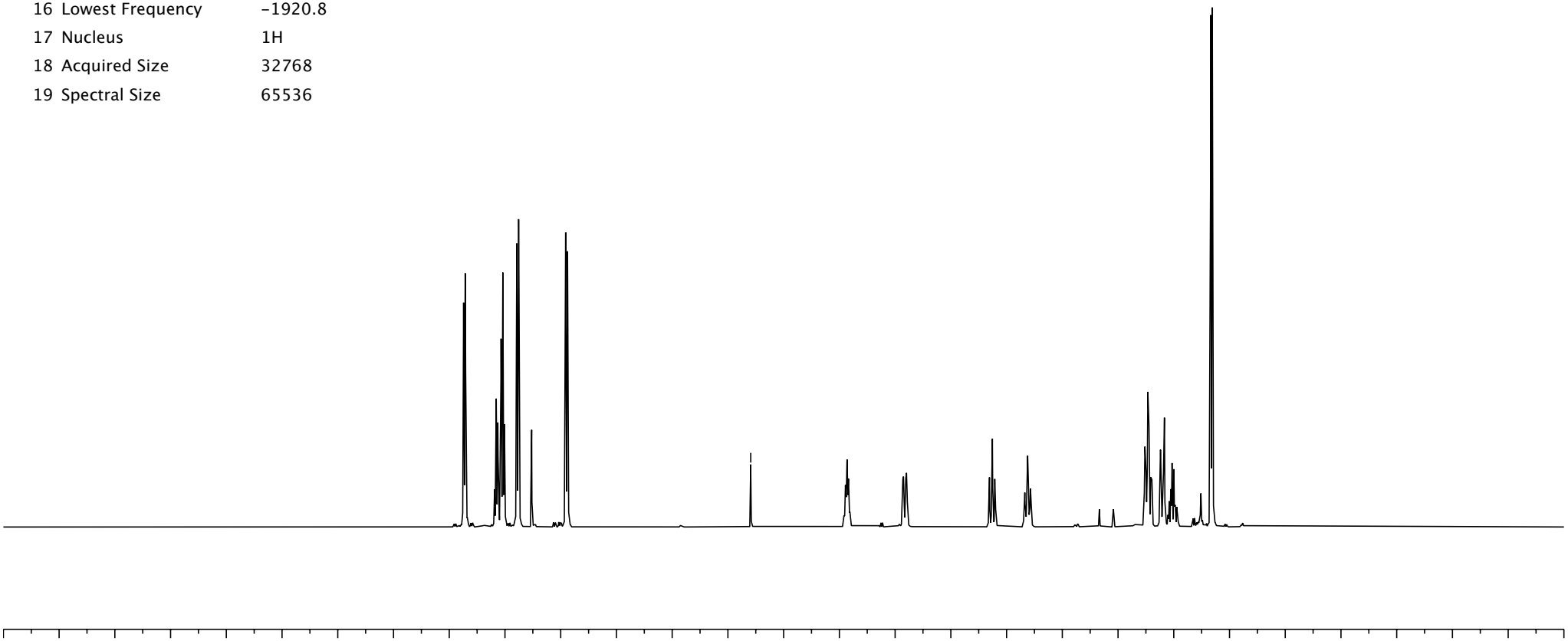


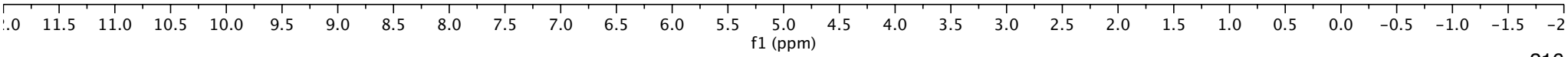


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2
10	Receiver Gain	69.2
11	Relaxation Delay	1.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

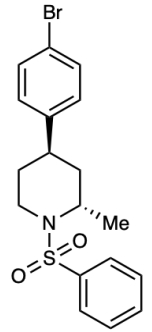
5.30 DCM

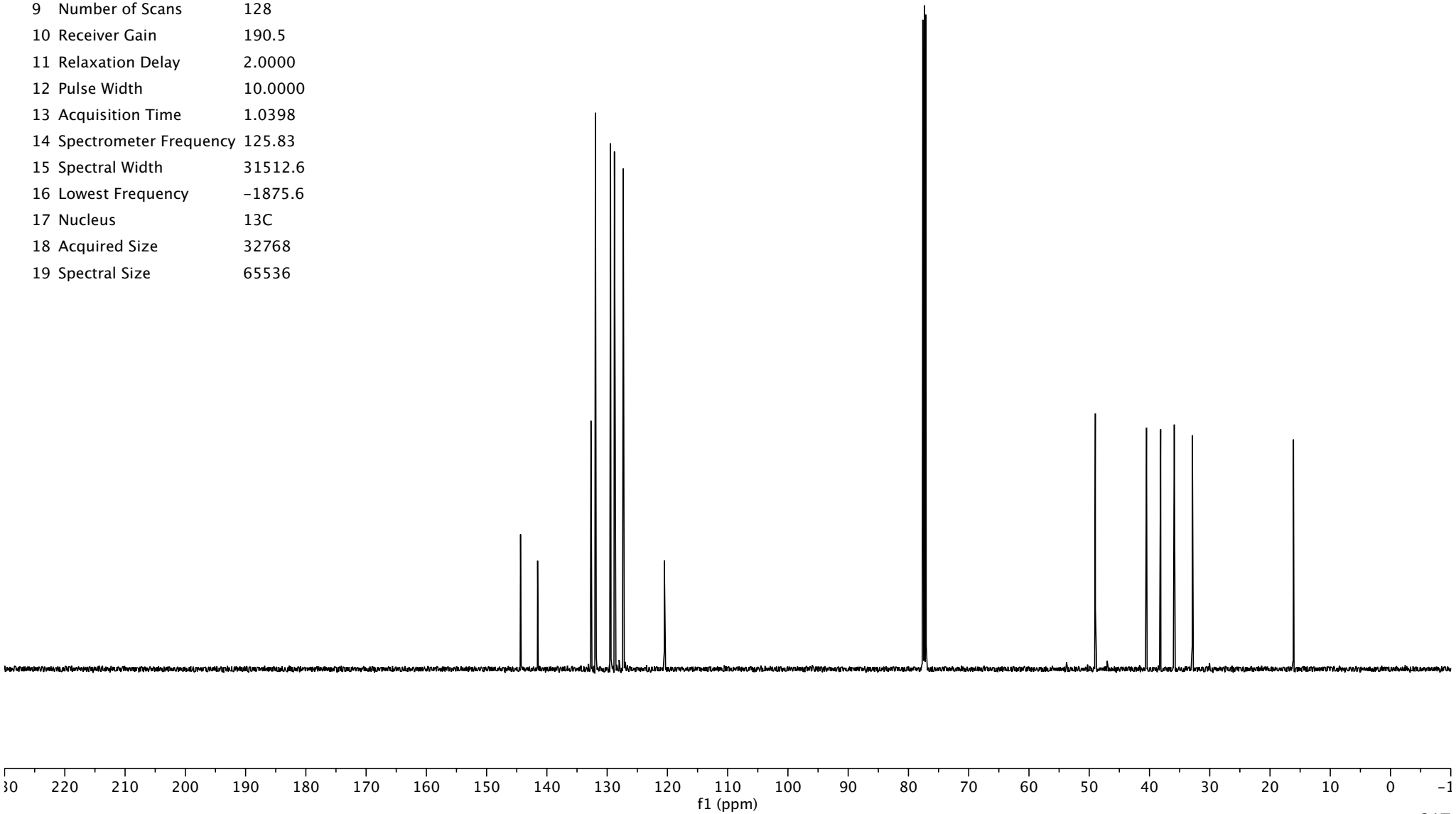


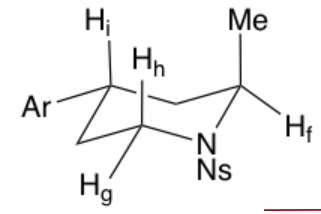


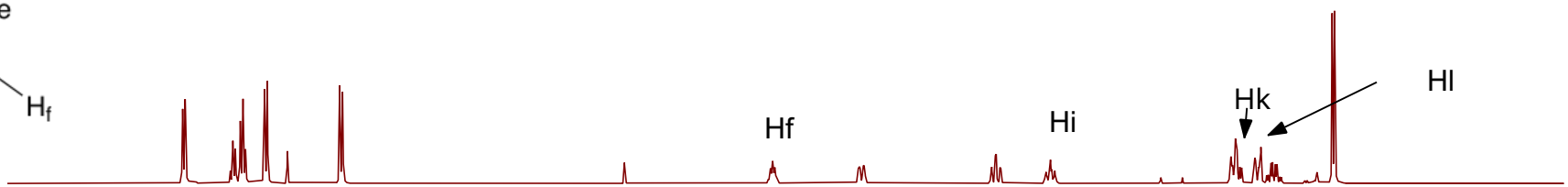


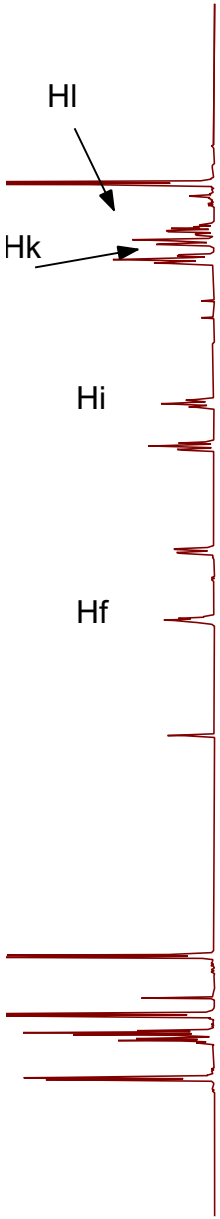
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	128
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1875.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



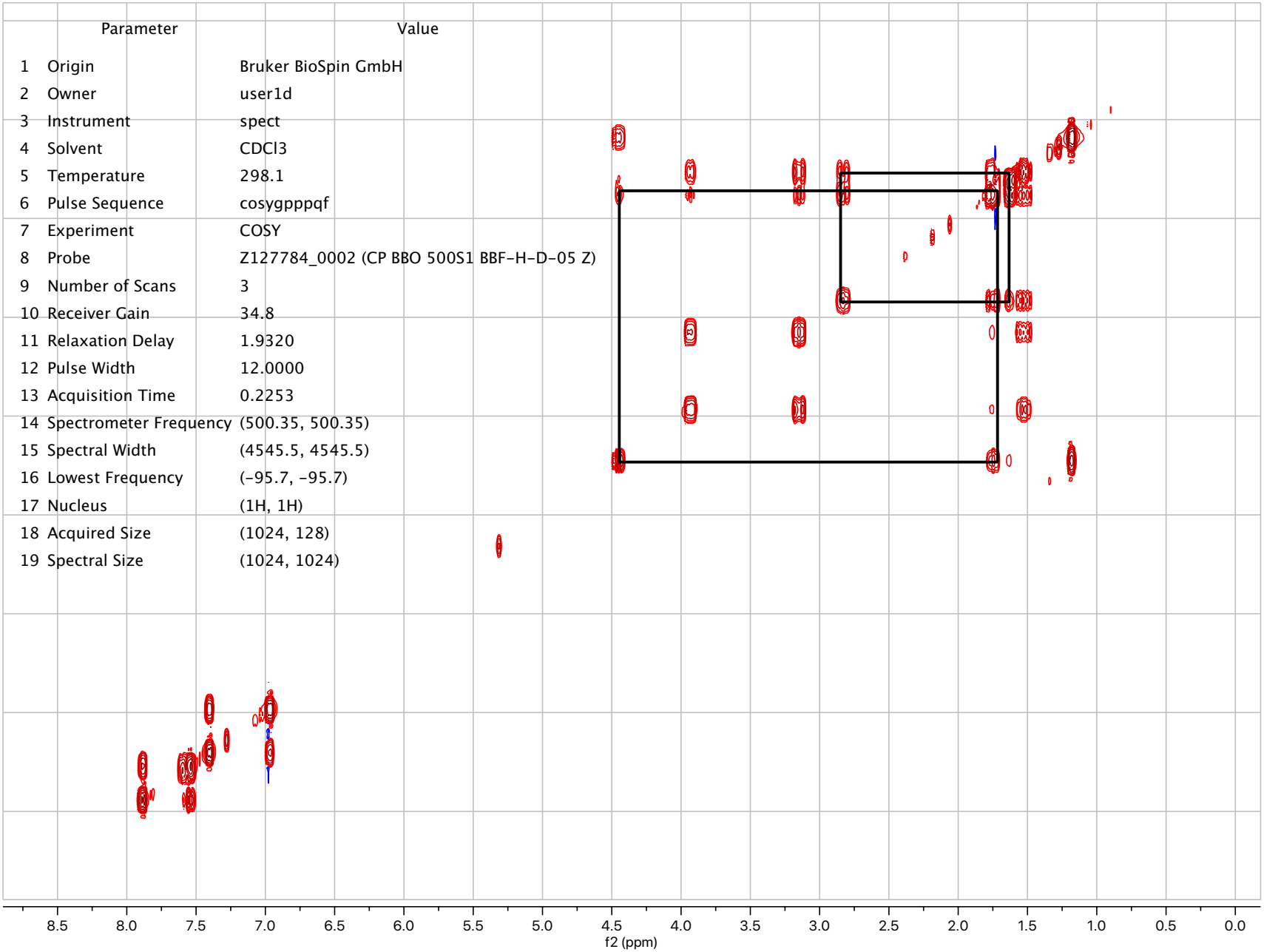


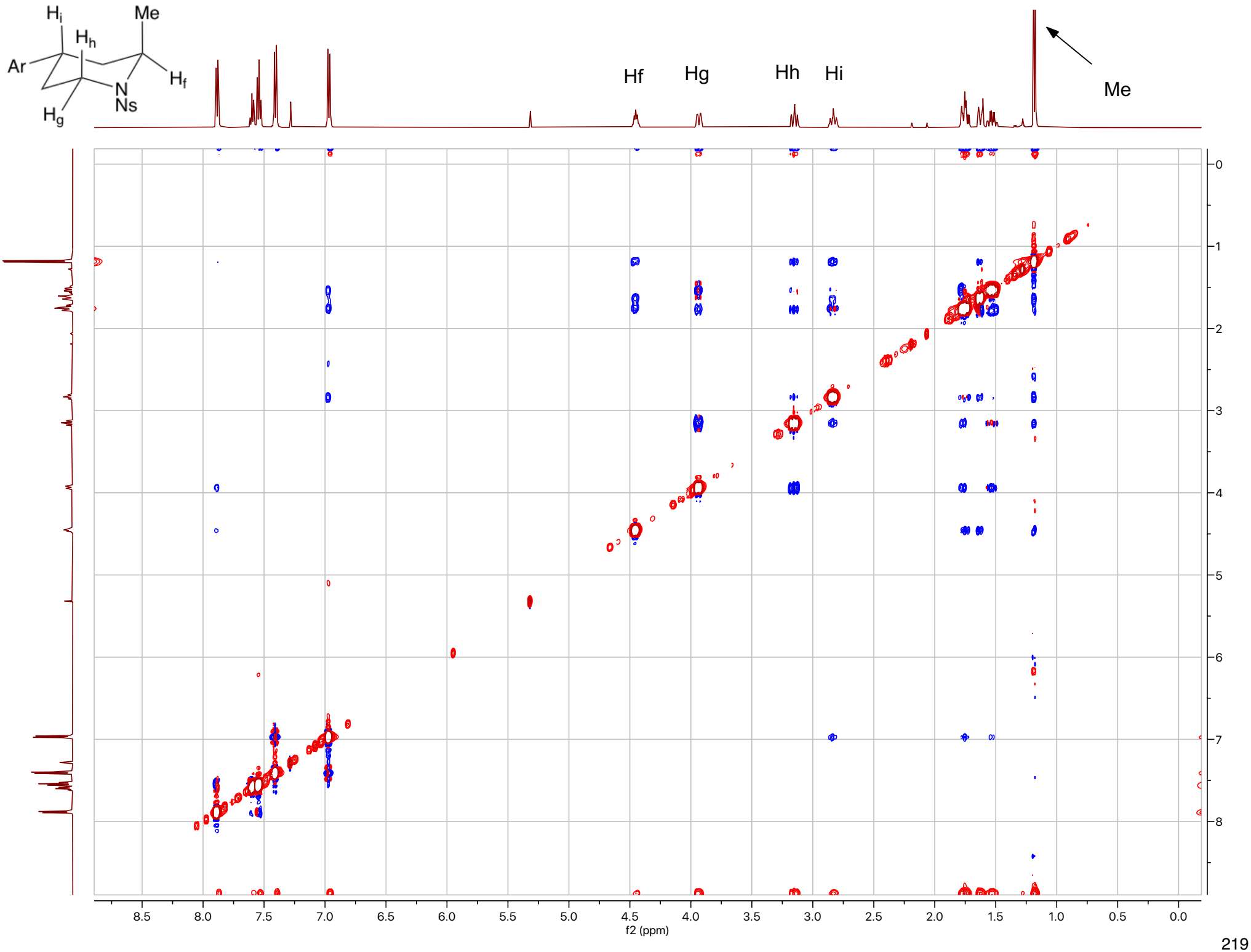


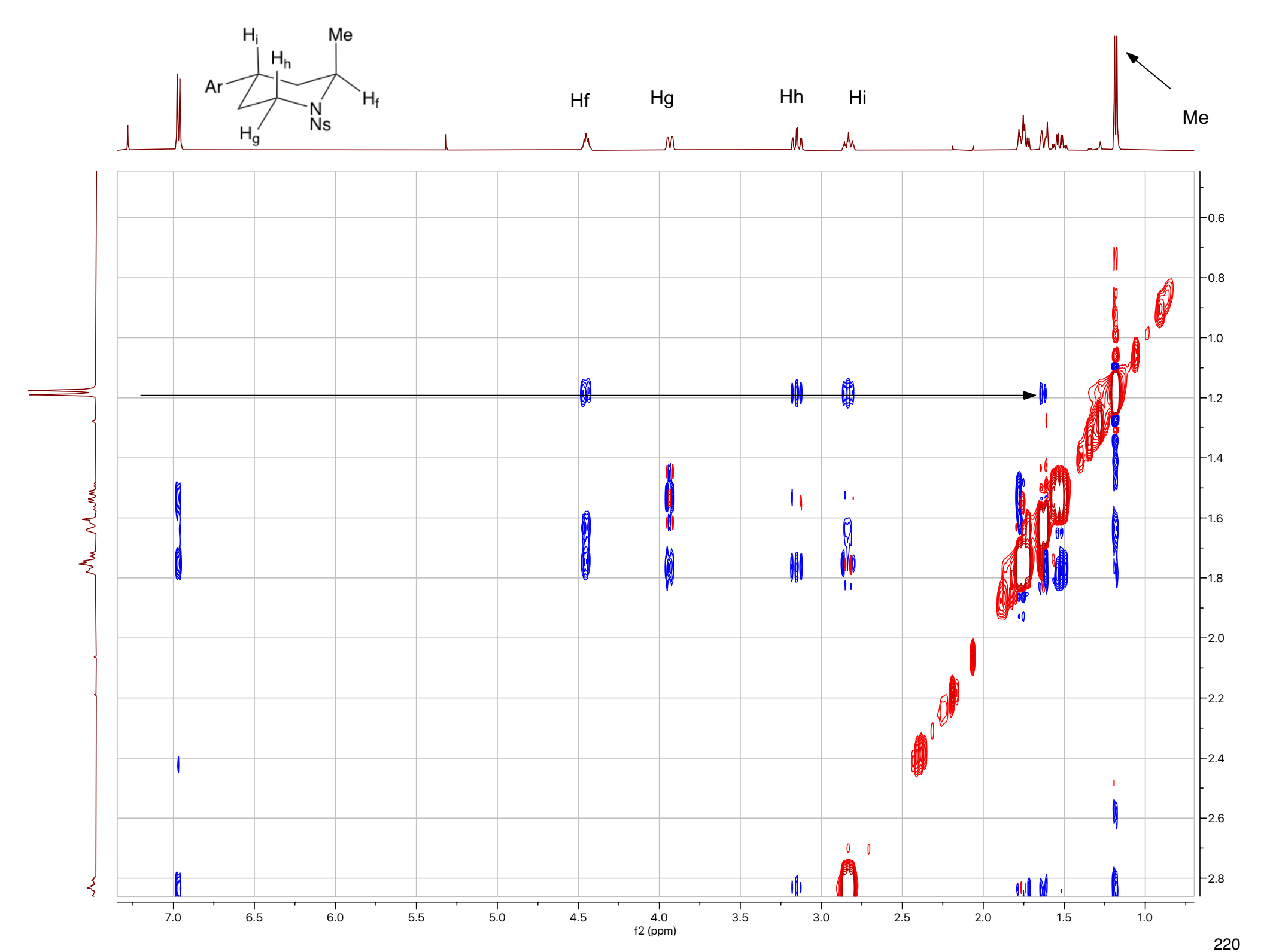




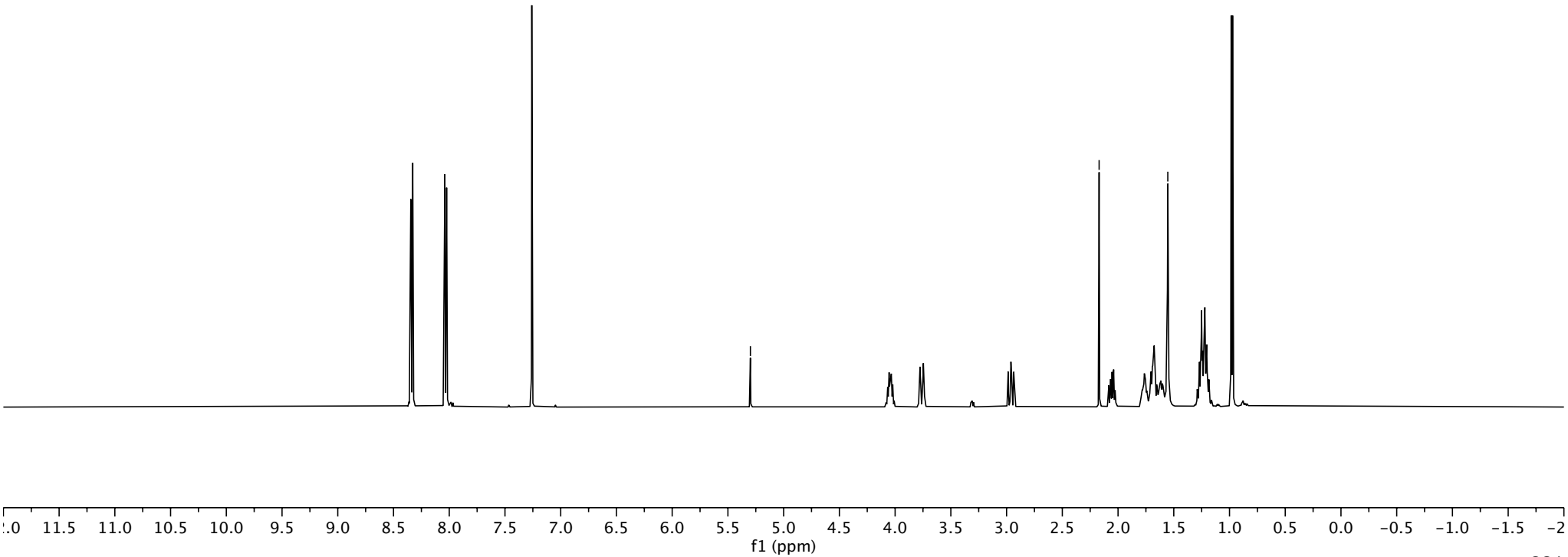
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	cosygpppqf
7	Experiment	COSY
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	3
10	Receiver Gain	34.8
11	Relaxation Delay	1.9320
12	Pulse Width	12.0000
13	Acquisition Time	0.2253
14	Spectrometer Frequency	(500.35, 500.35)
15	Spectral Width	(4545.5, 4545.5)
16	Lowest Frequency	(-95.7, -95.7)
17	Nucleus	(1H, 1H)
18	Acquired Size	(1024, 128)
19	Spectral Size	(1024, 1024)



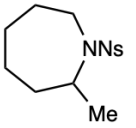

Hi
Me
Hh
Ar
Hf
N
Ns
Hg
Hf
Hg
Hh
Hi
Me
f2 (ppm)


Hi
Me
Hh
Ar
Hf
N
Ns
Hg
Hf
Hg
Hh
Hi
Me
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

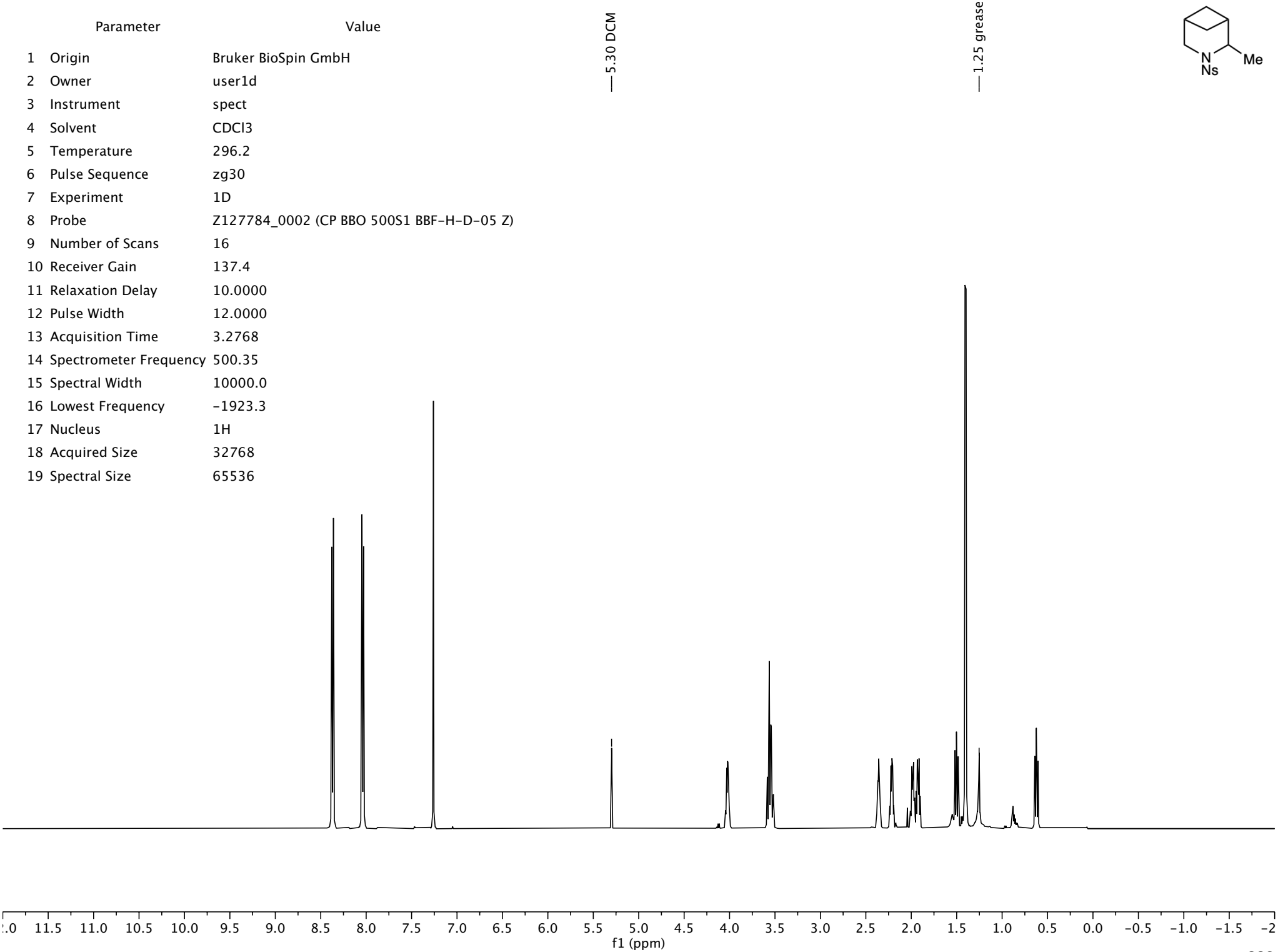
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	168.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1760.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



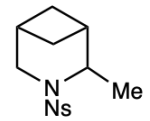
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1873.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

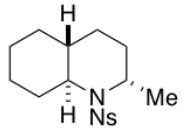


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	137.4
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1923.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

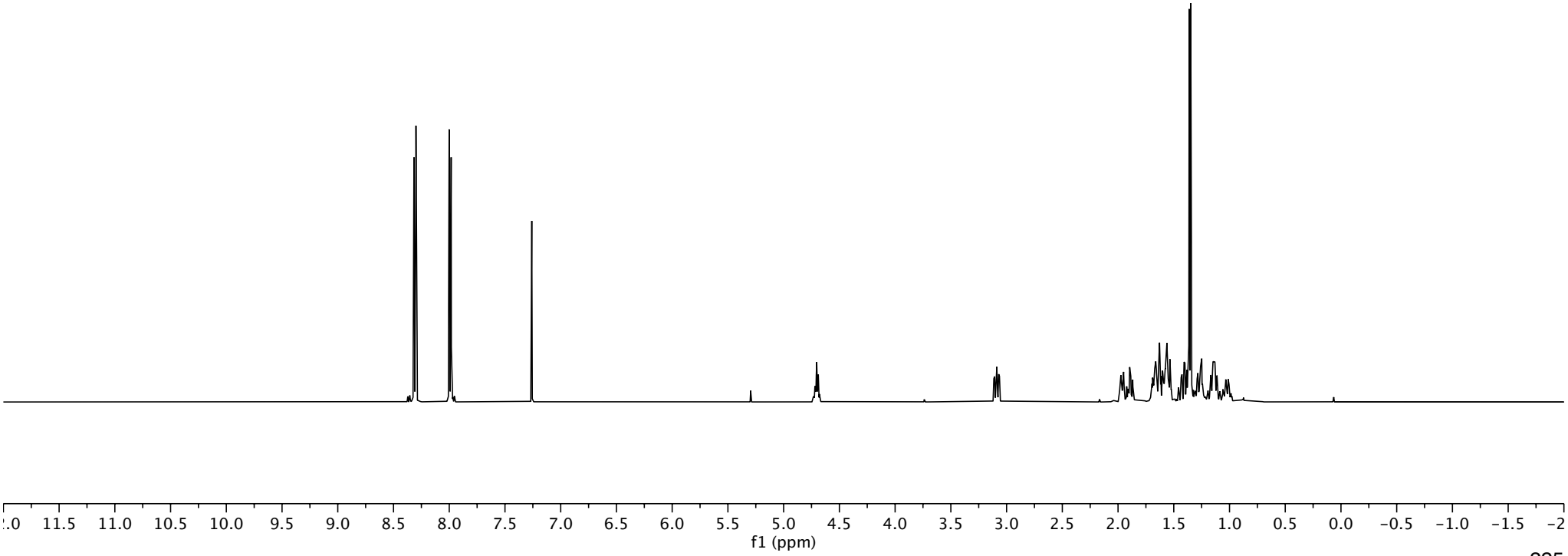


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1886.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

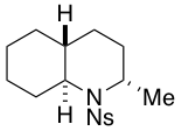


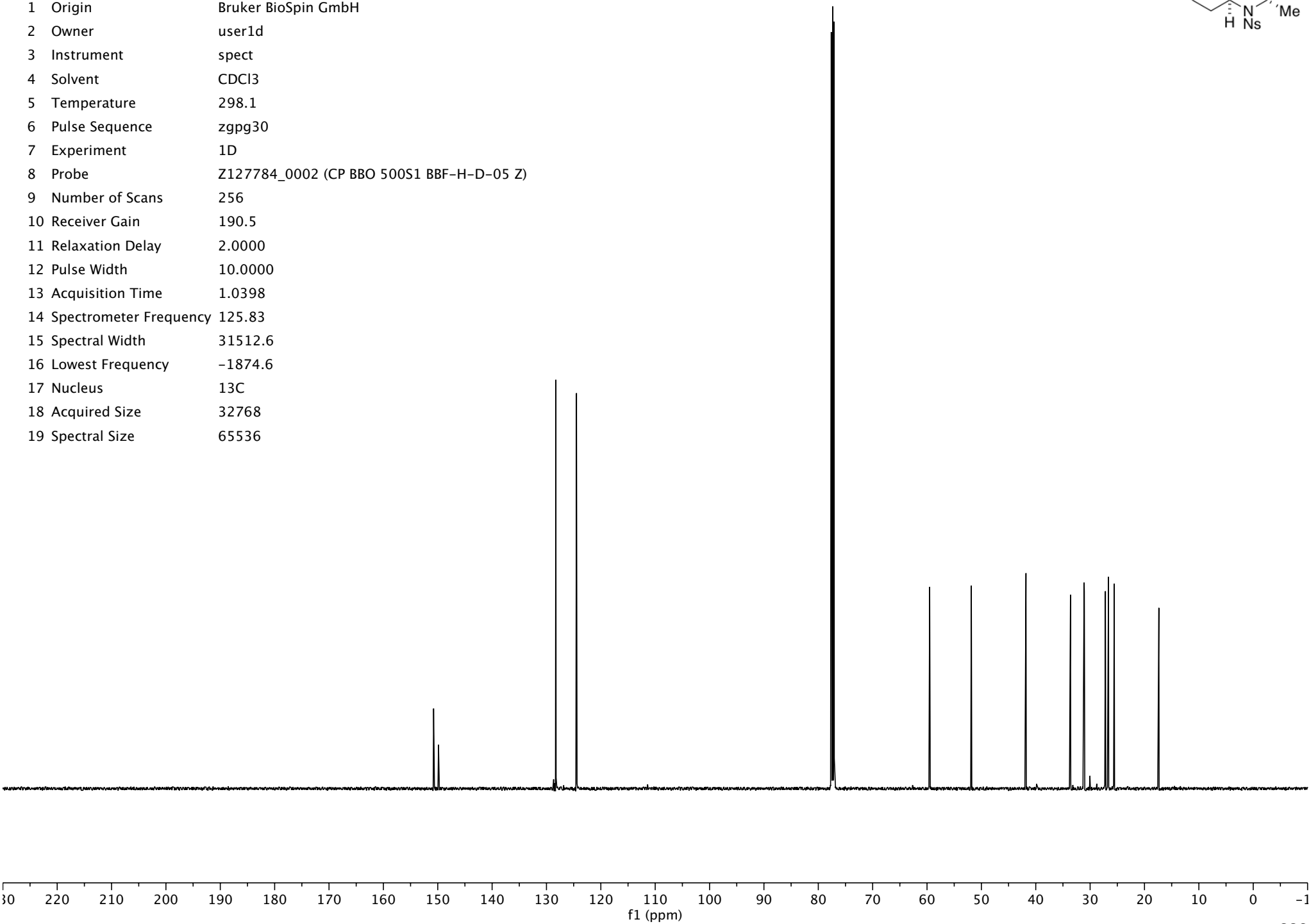


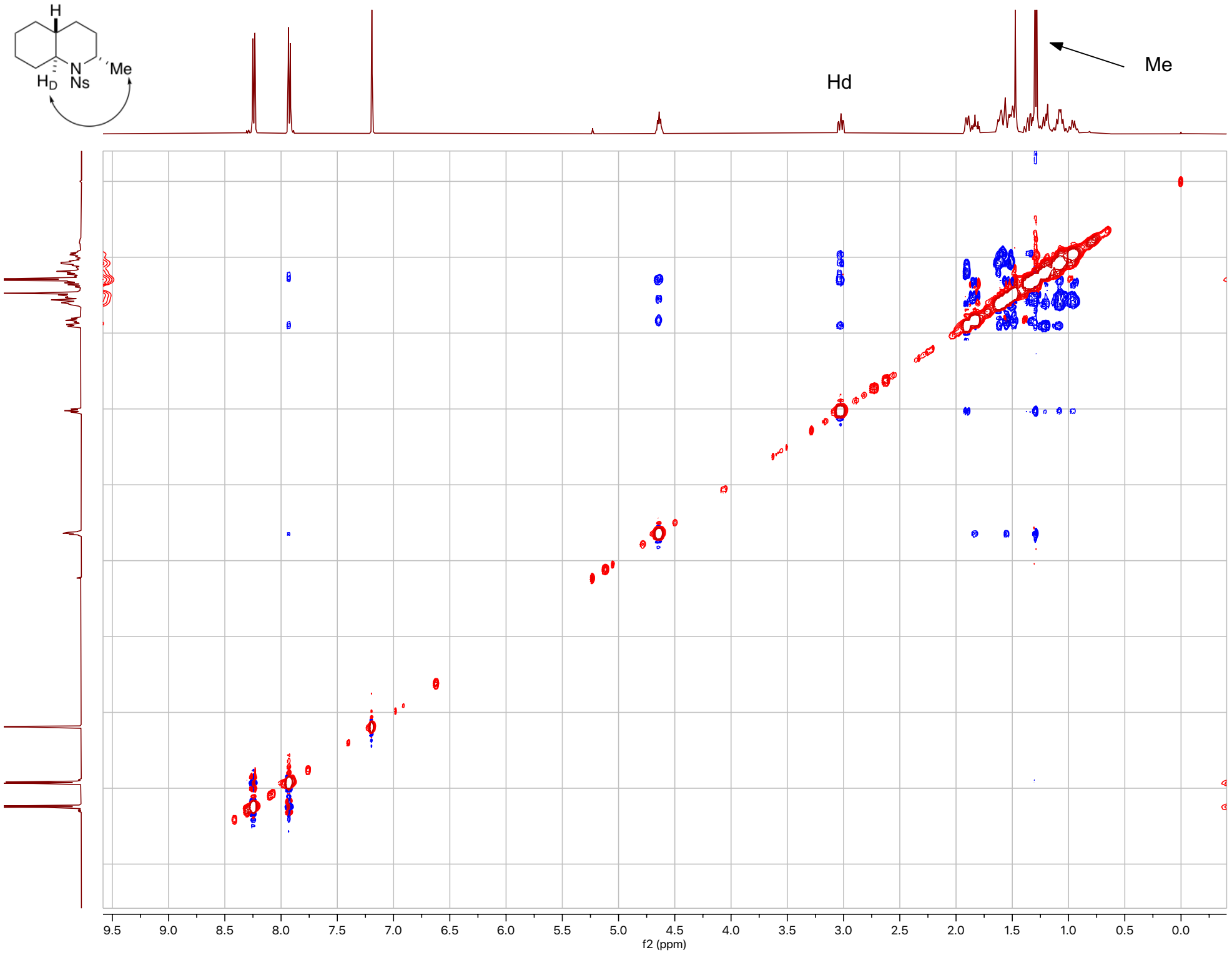
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.5
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

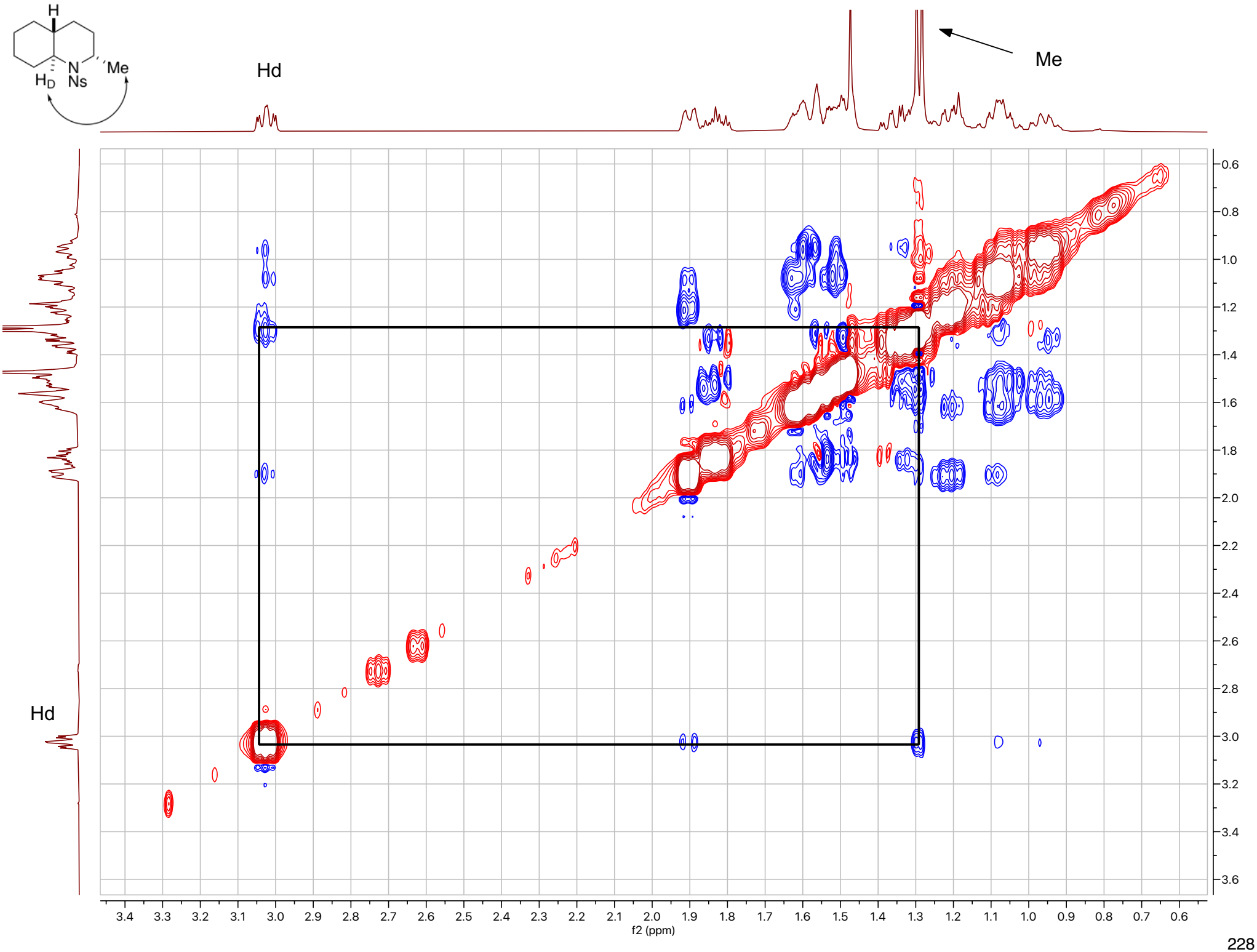


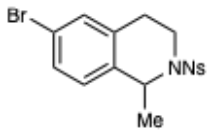
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



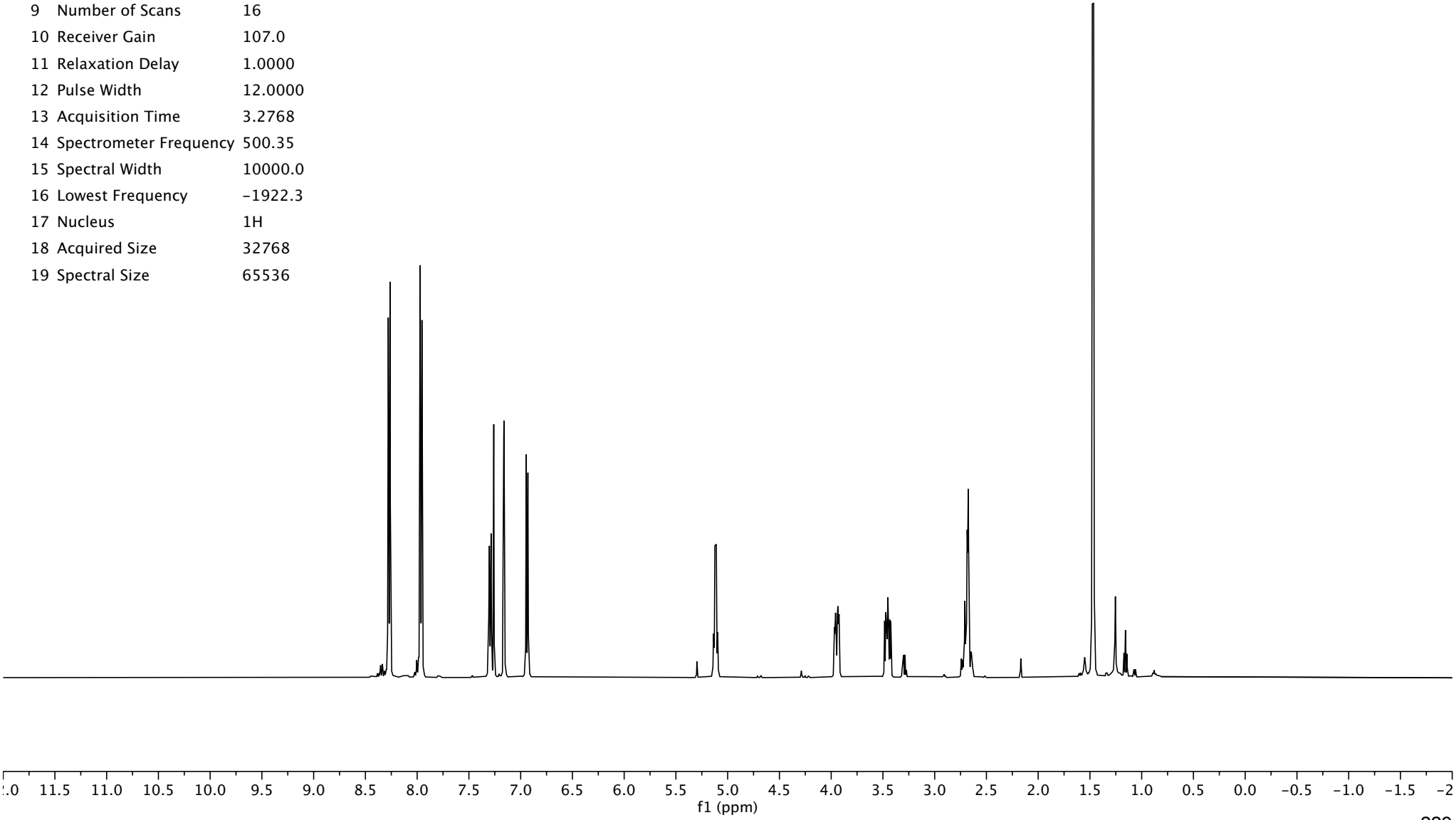


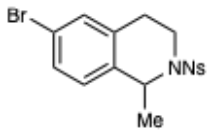

H
N
Me
H_D
Ns
Hd
Me
f2 (ppm)


H
N
Me
H_D
Ns
Hd
Me
Hd
f2 (ppm)

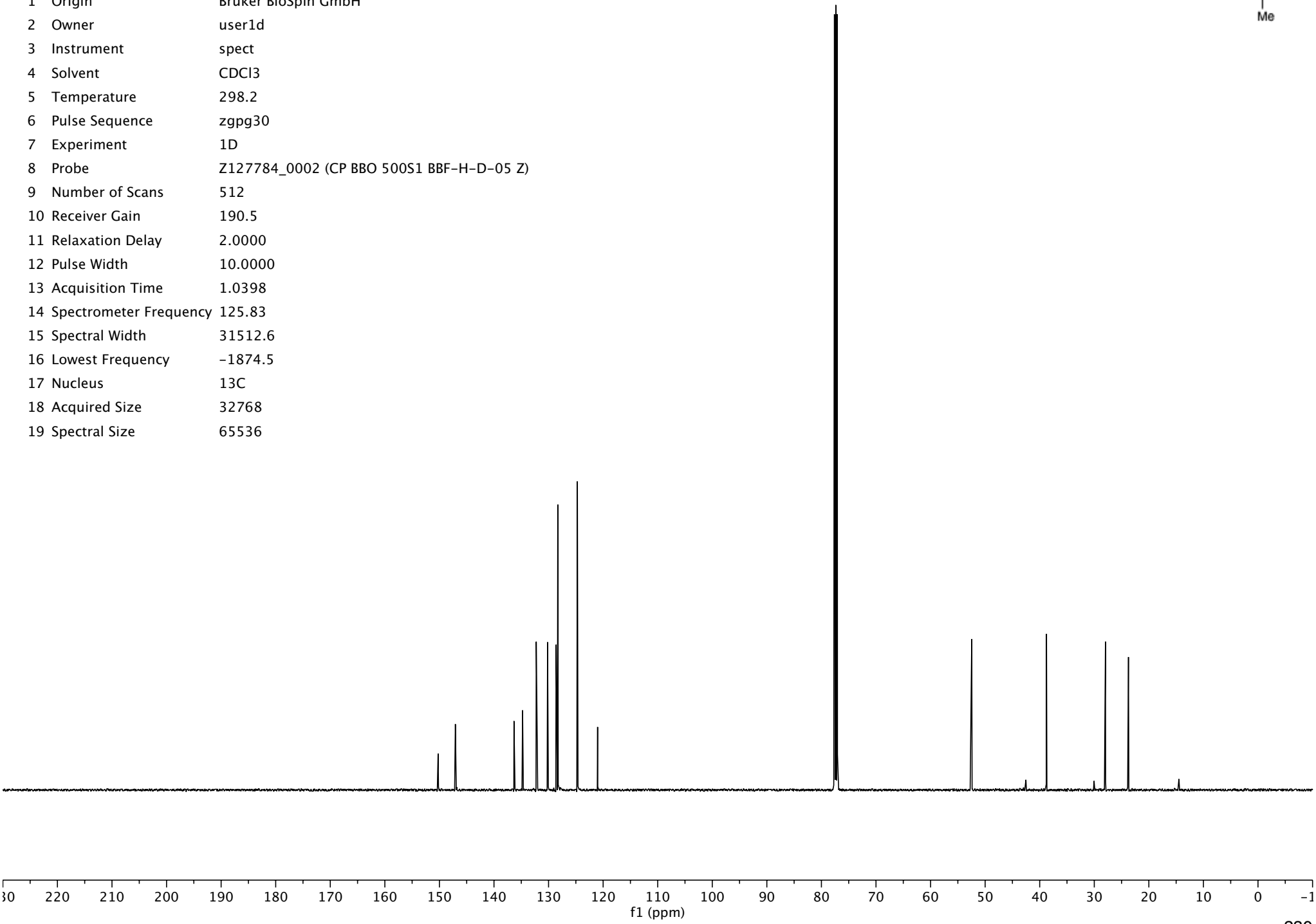


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	107.0
11	Relaxation Delay	1.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

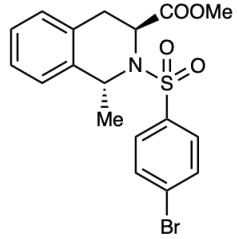


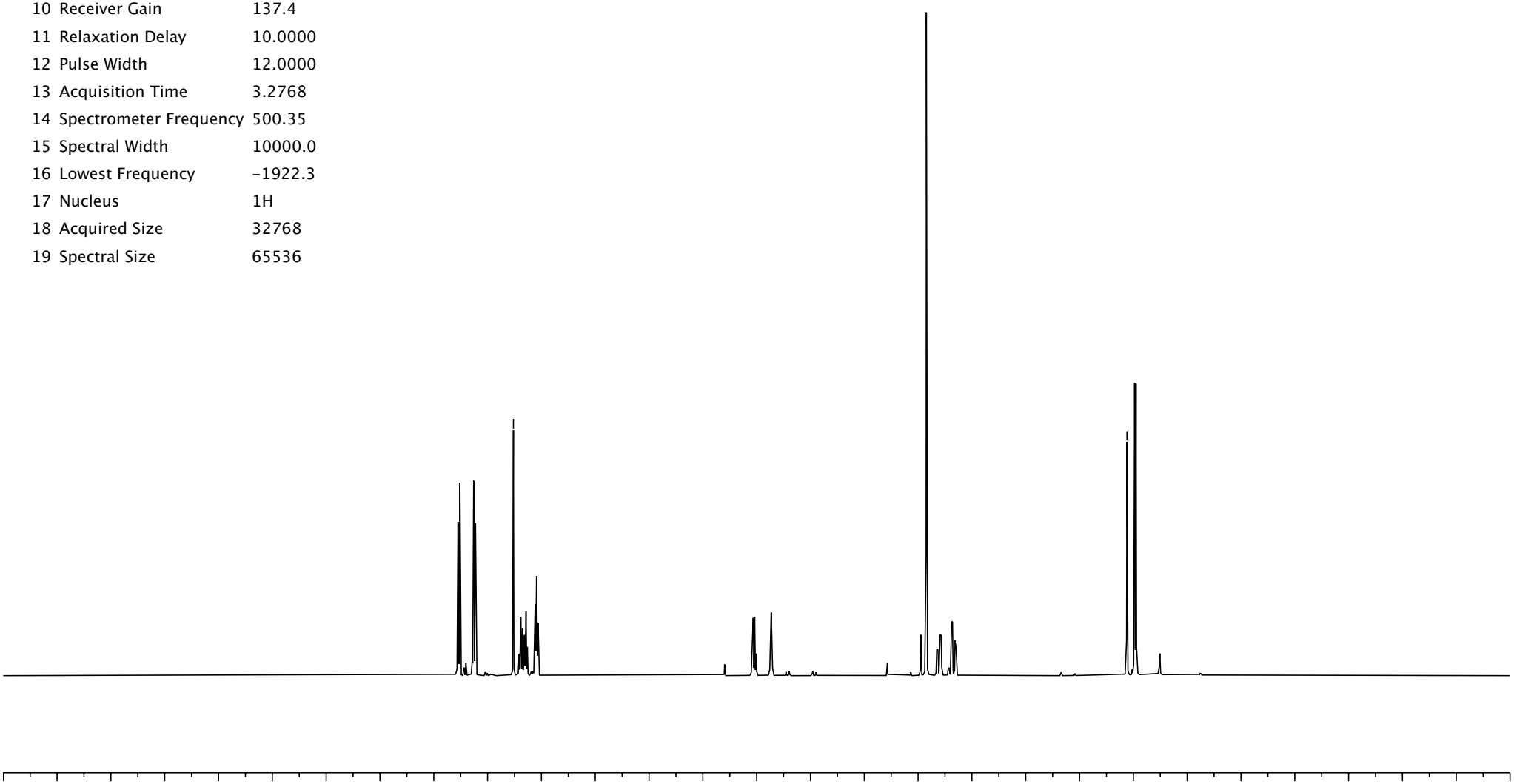


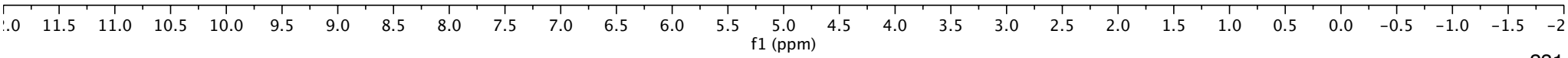
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1874.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



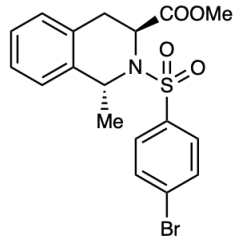
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	137.4
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

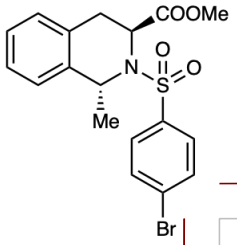




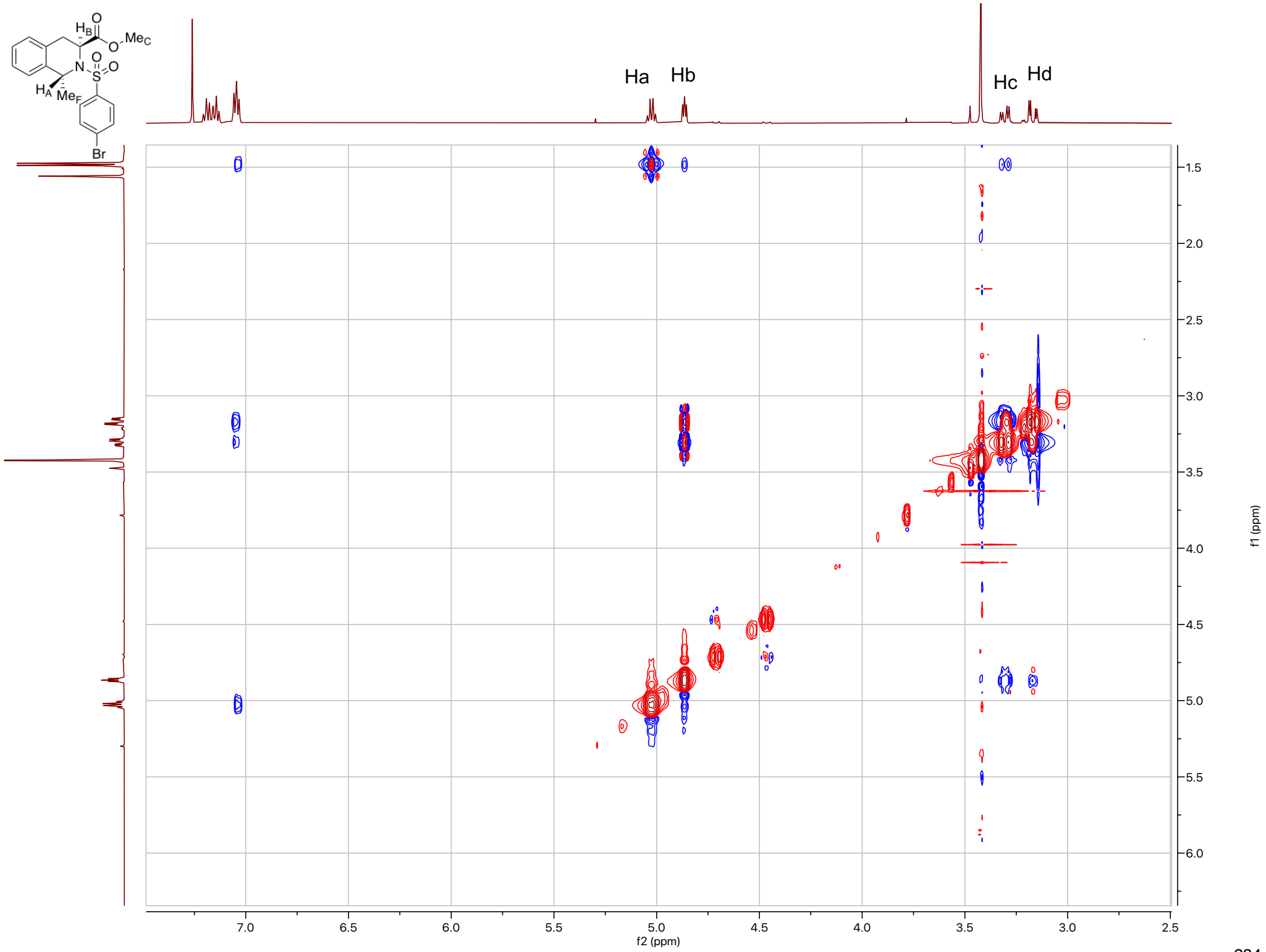


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1887.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

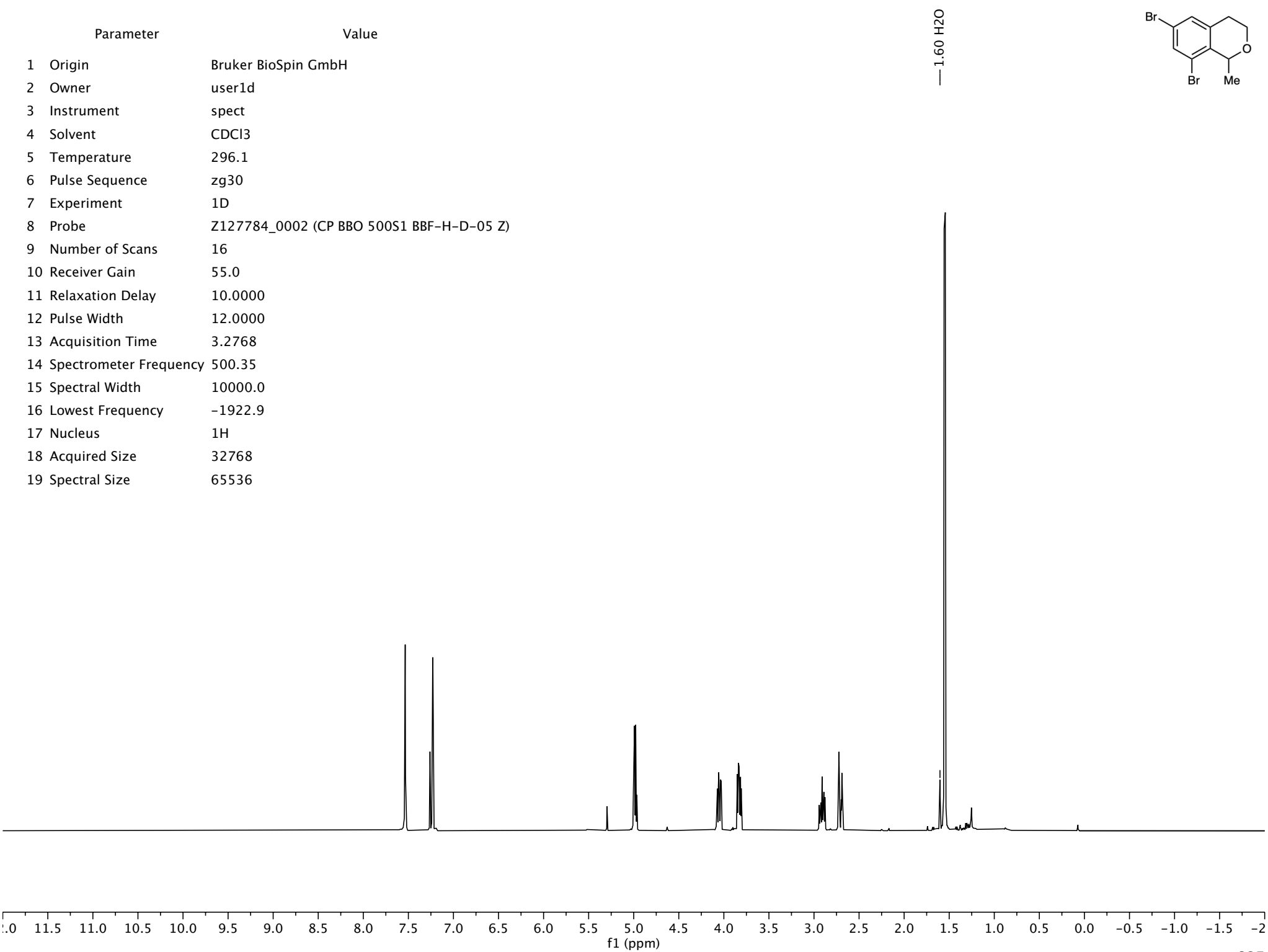


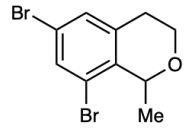


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	noesygpphpp
6	Experiment	NOESY
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	4
9	Receiver Gain	29.7
10	Relaxation Delay	2.0000
11	Pulse Width	12.0000
12	Acquisition Time	0.2048
13	Spectrometer Frequency	(500.35, 500.35)
14	Spectral Width	(5000.0, 5000.0)
15	Lowest Frequency	(-160.9, -158.9)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 256)
18	Spectral Size	(1024, 1024)

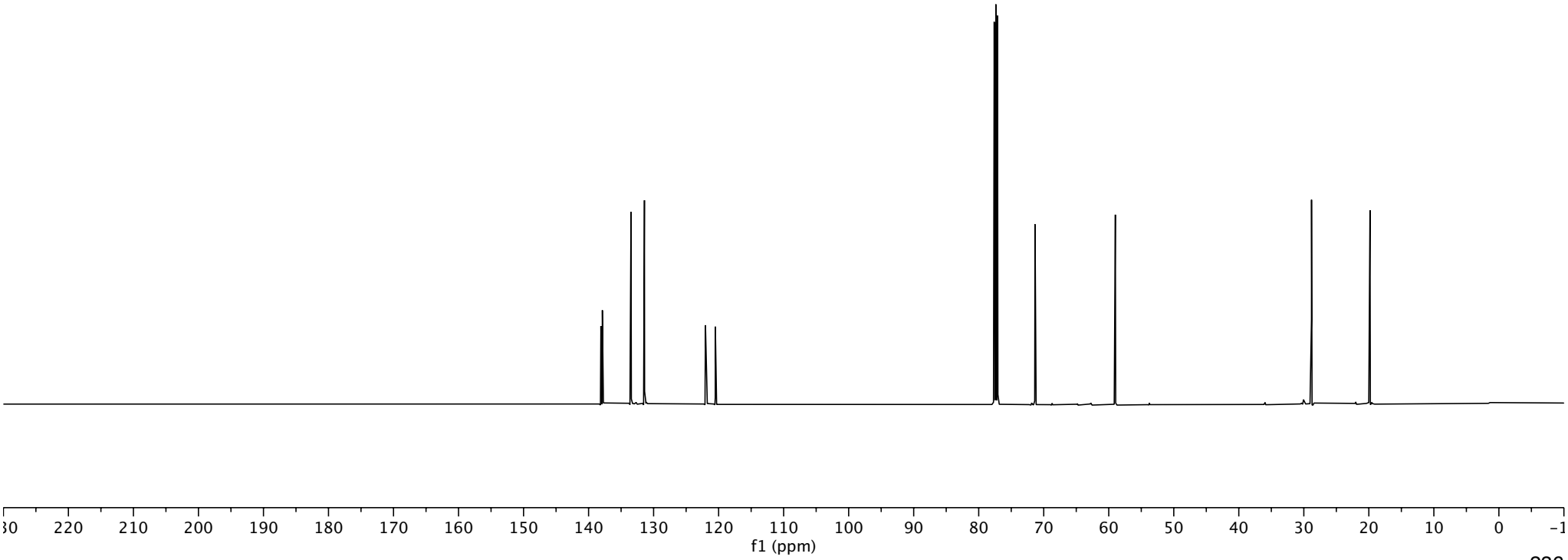

Ha
Hb
Hc
Hd
Br
f2 (ppm)
f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

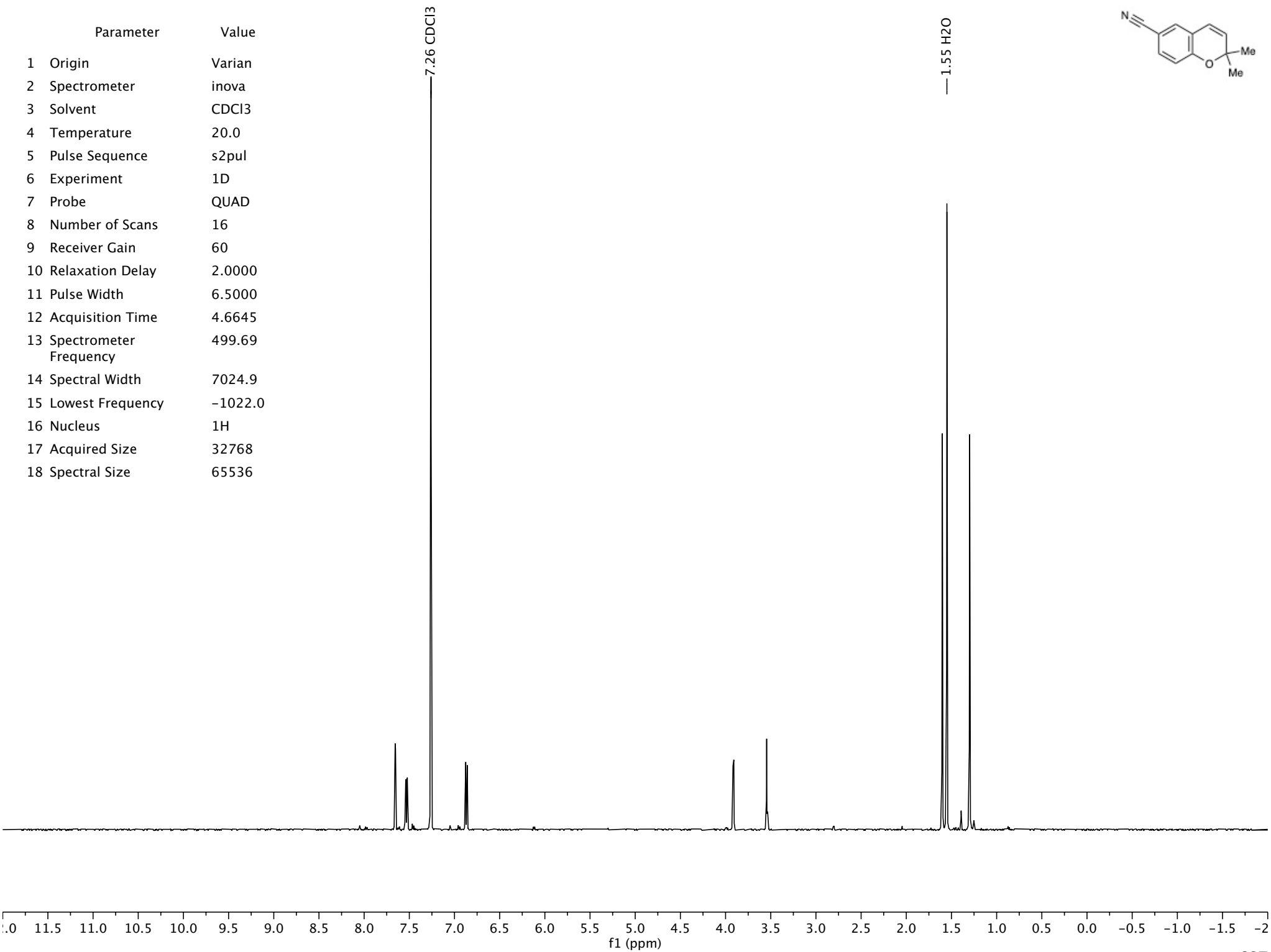




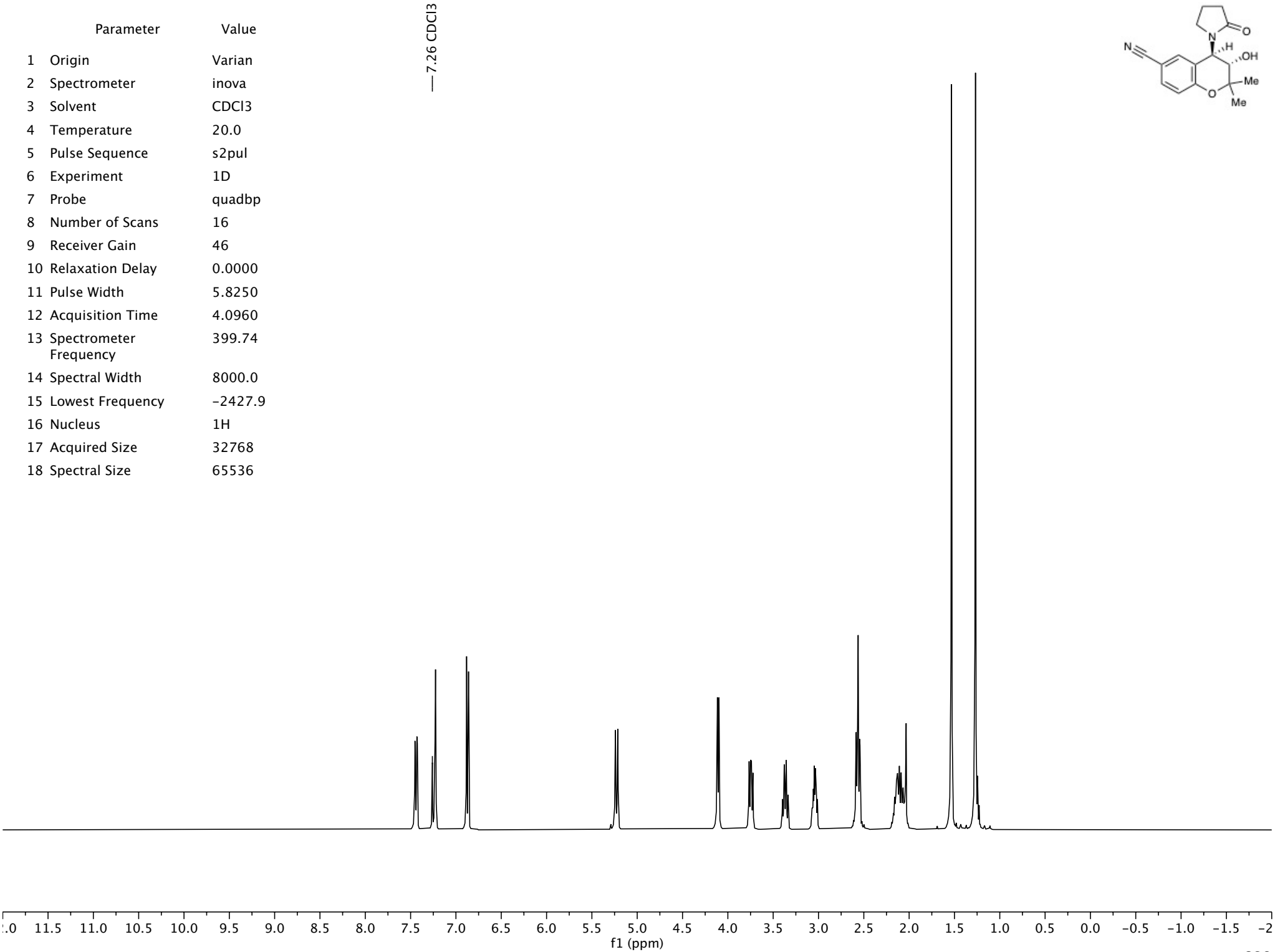
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1876.1
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



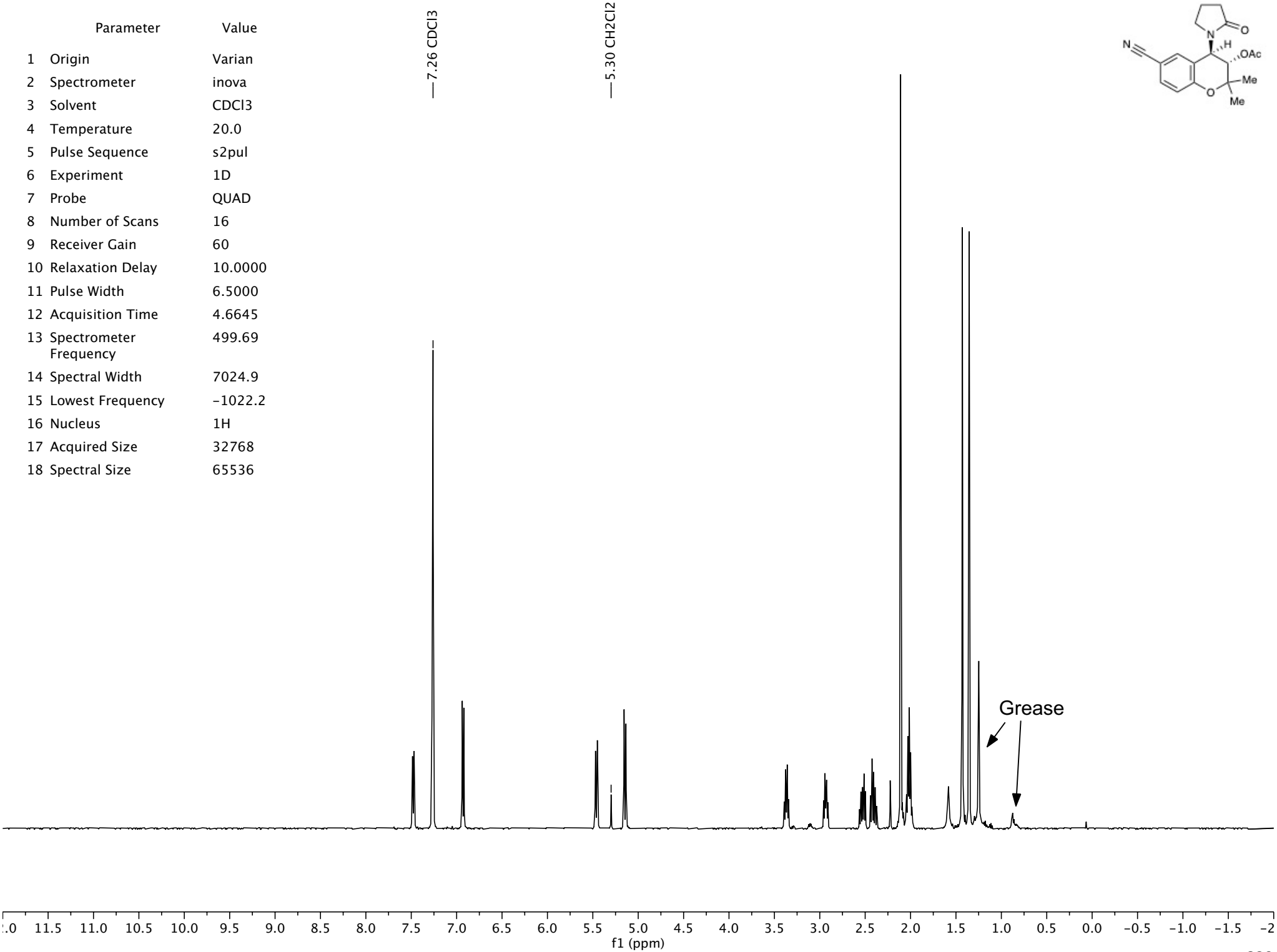
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1022.0
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



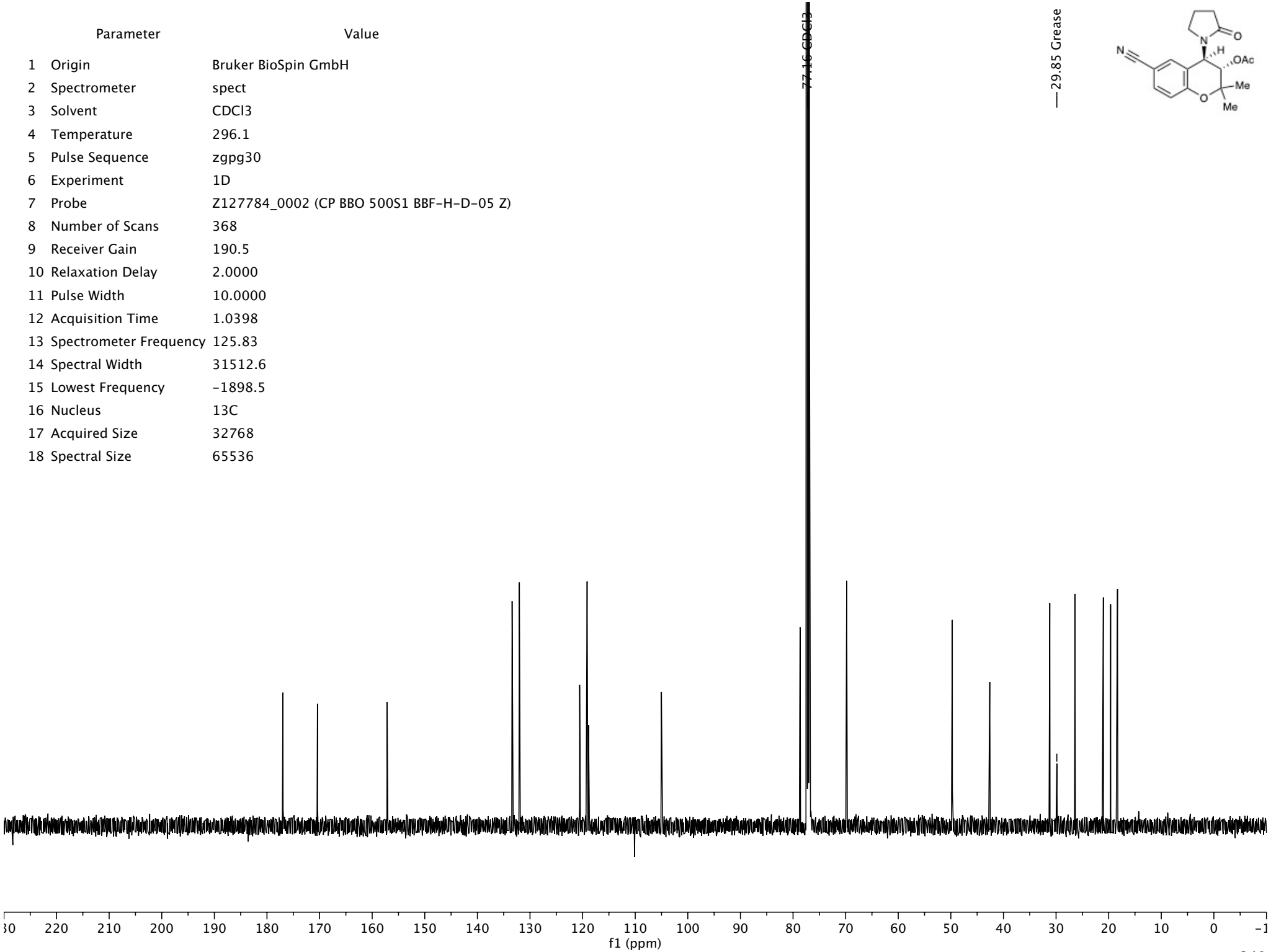
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	46
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2427.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



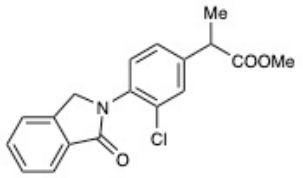
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1022.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

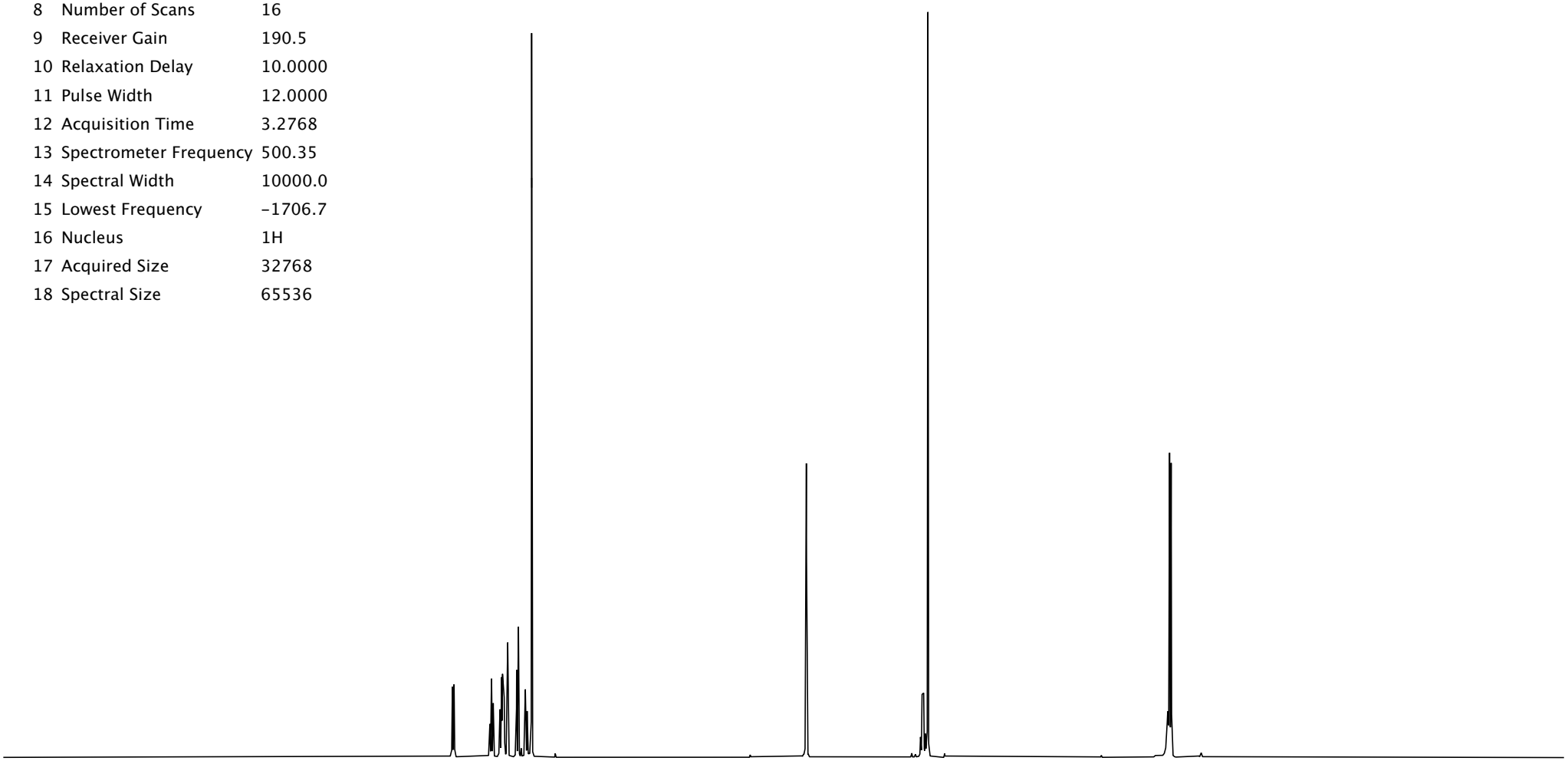


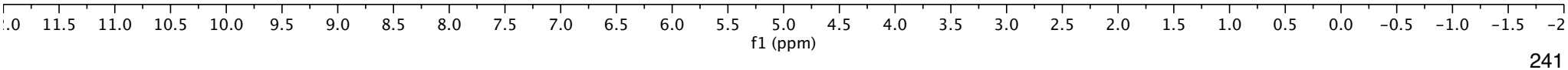
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



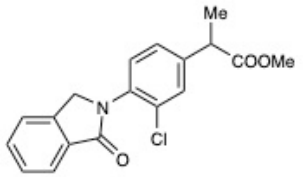
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1706.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



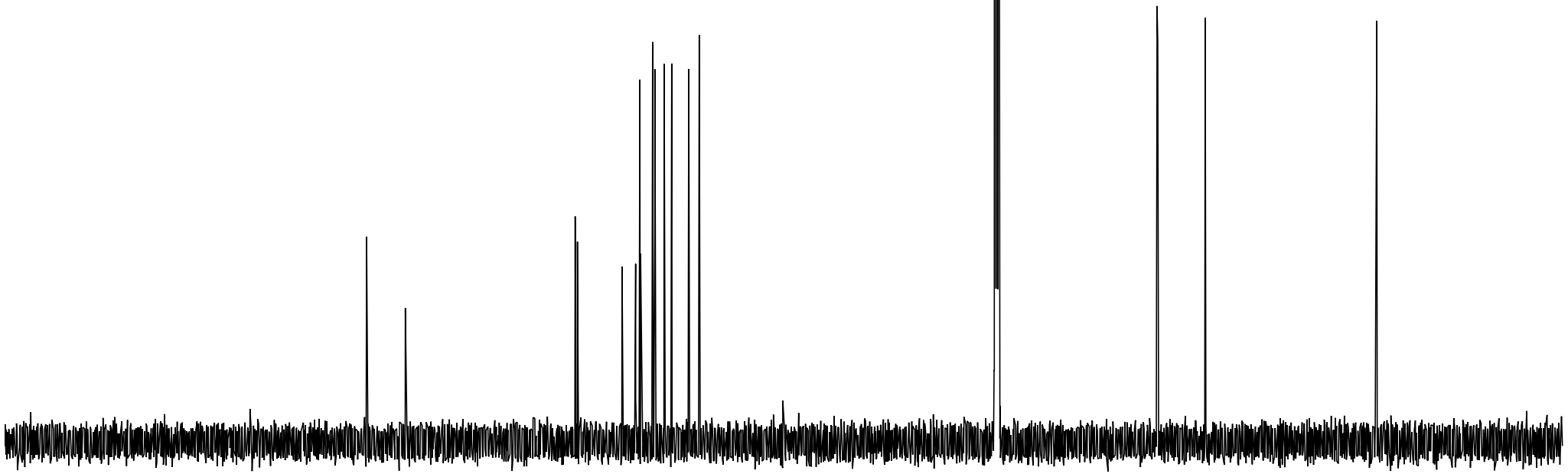




	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.7
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



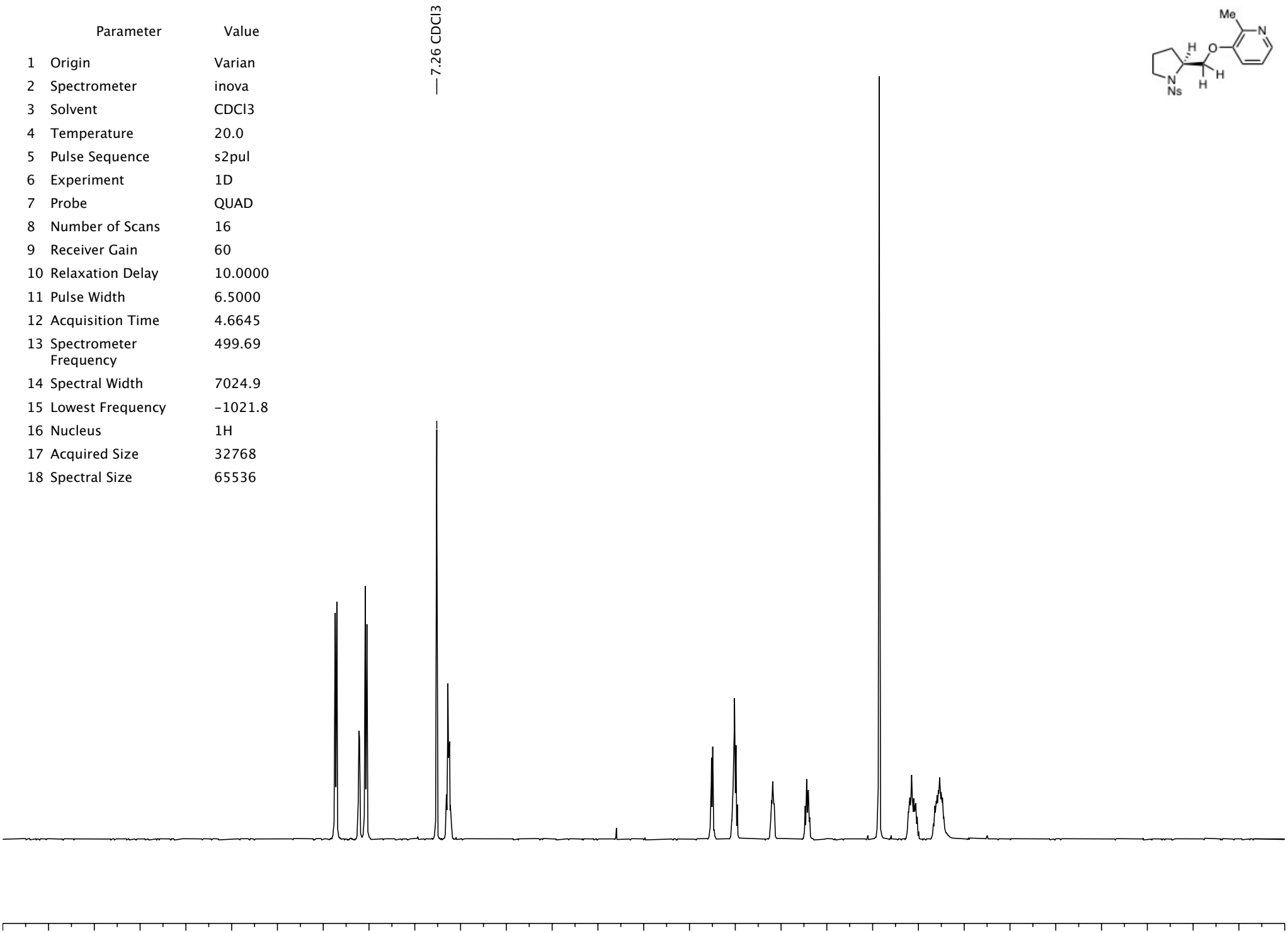
77.16 CDCl3



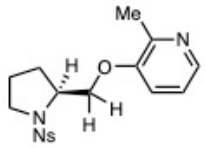
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

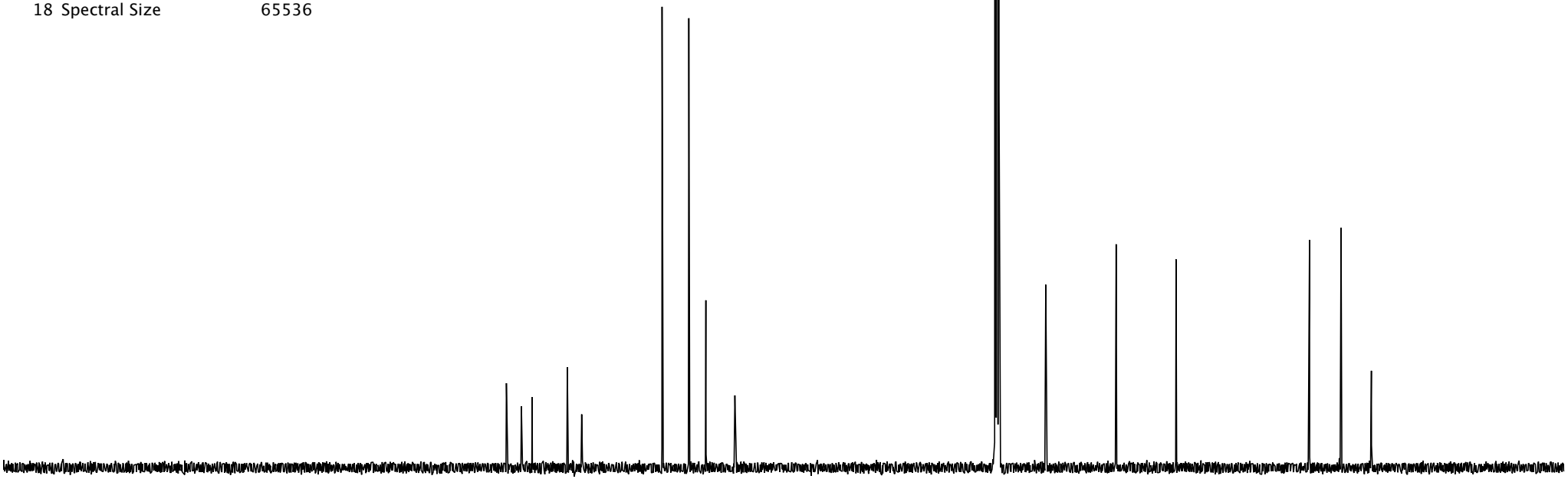
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1021.8
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

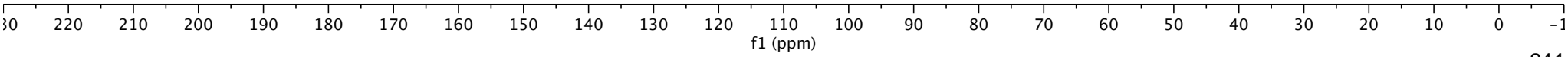


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	640
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

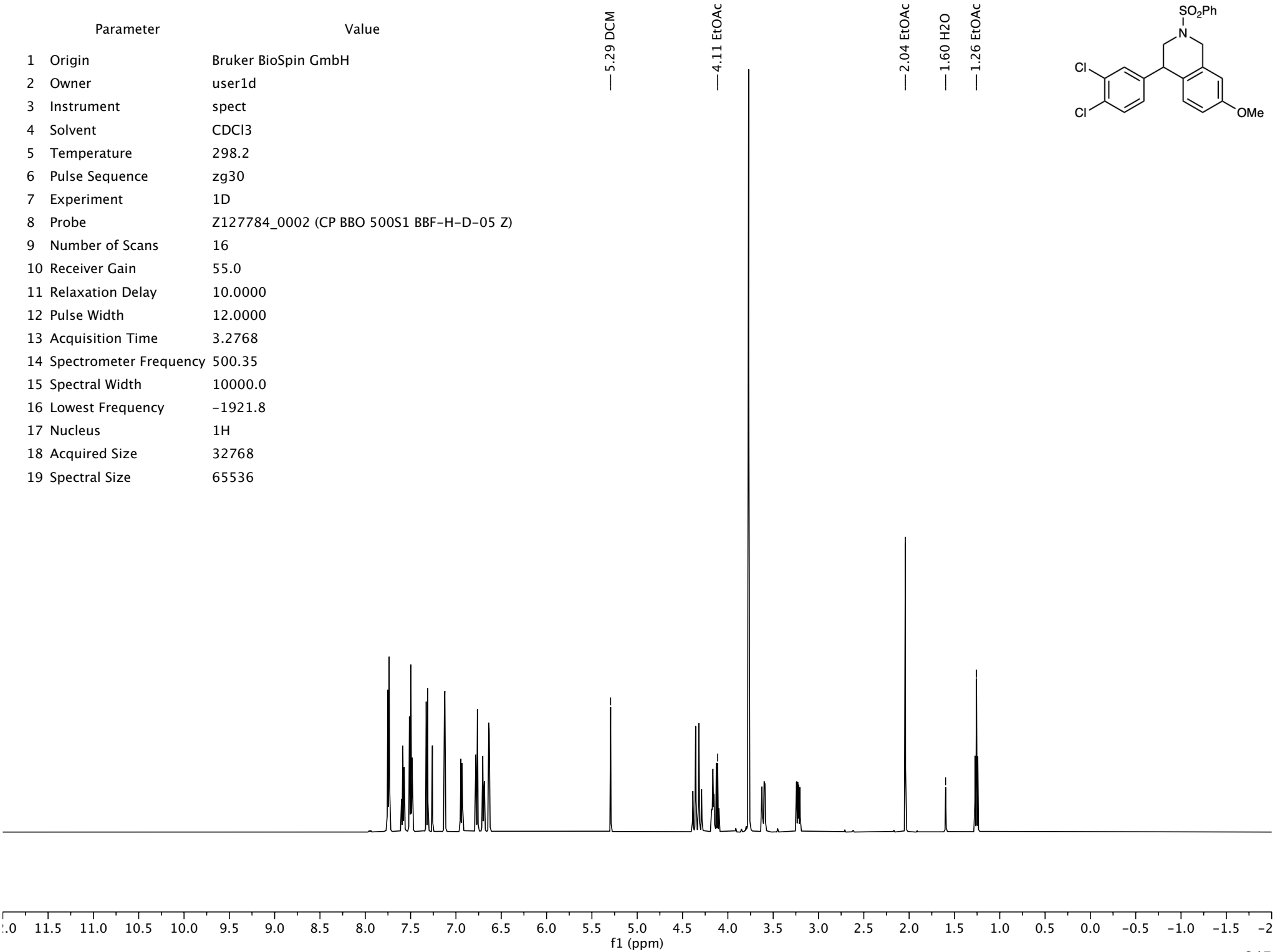


77.16 CDCl3

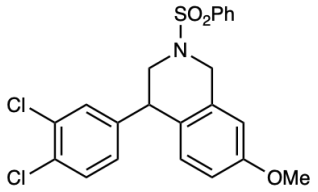


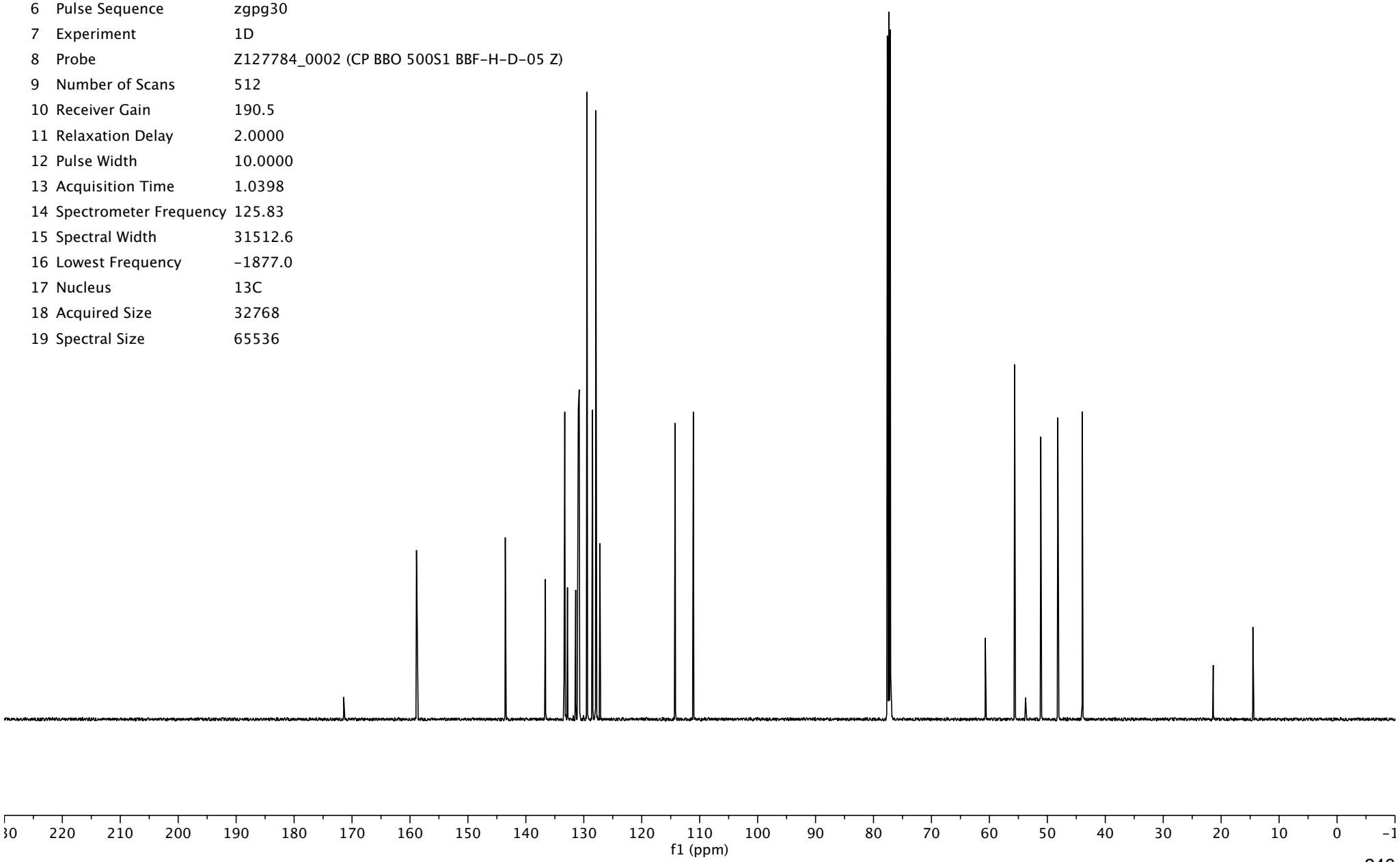


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1921.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

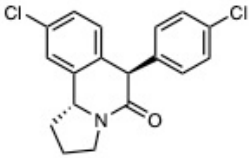


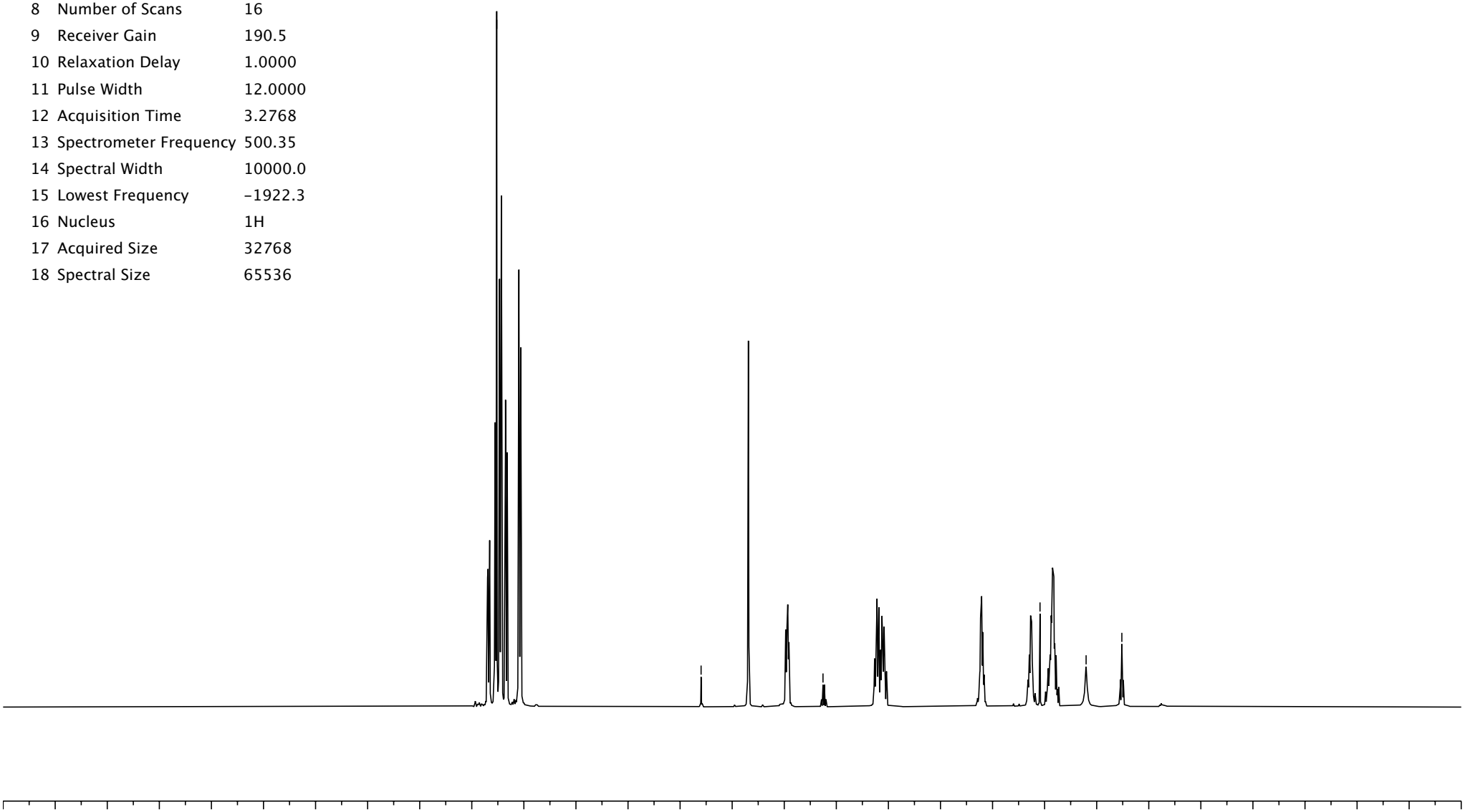
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1877.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

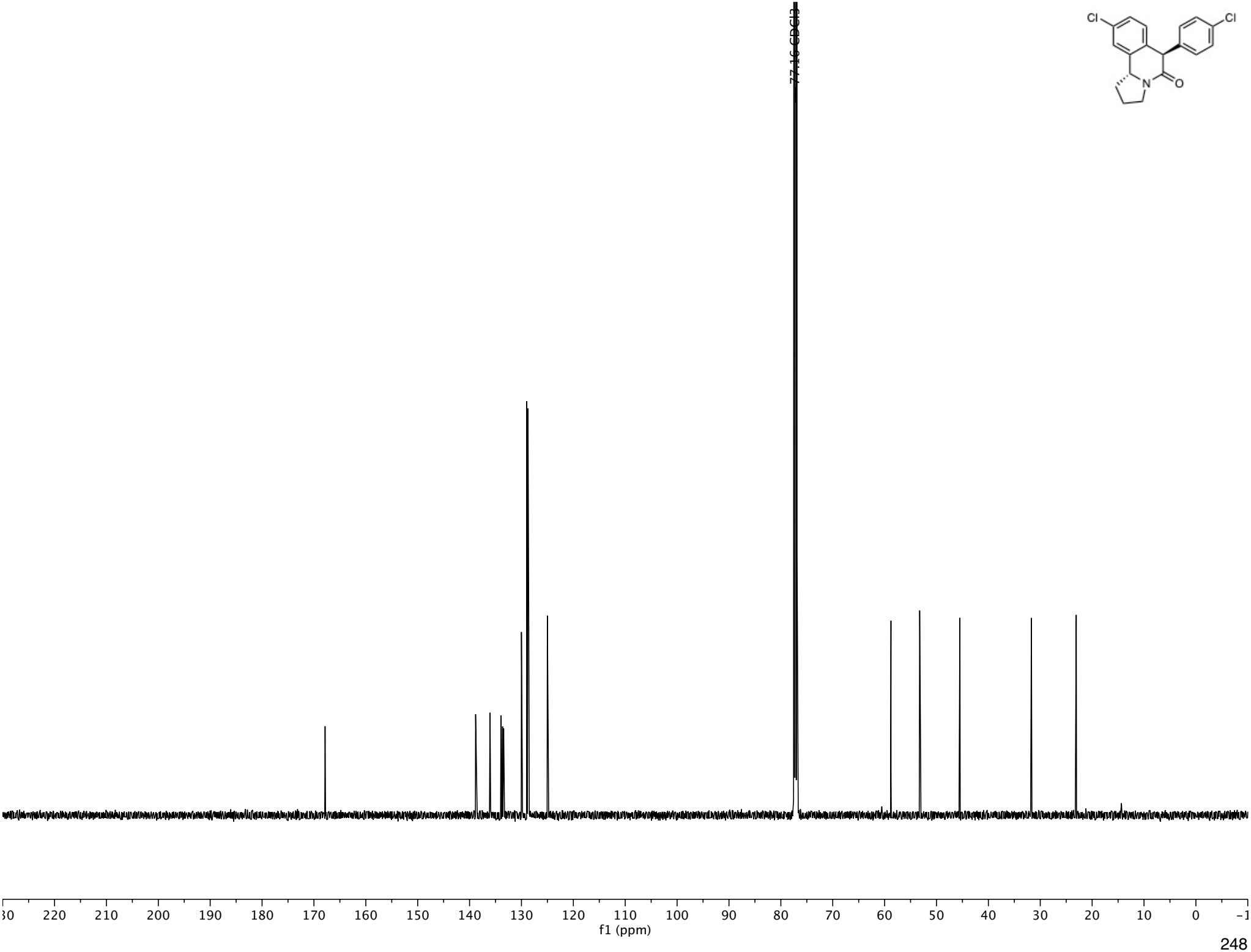


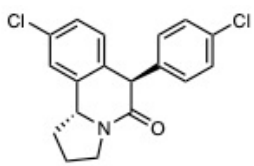


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.3
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

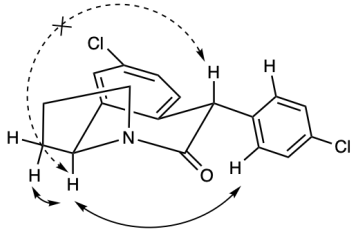





77.16 CDCl3
Cl
Cl
N
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



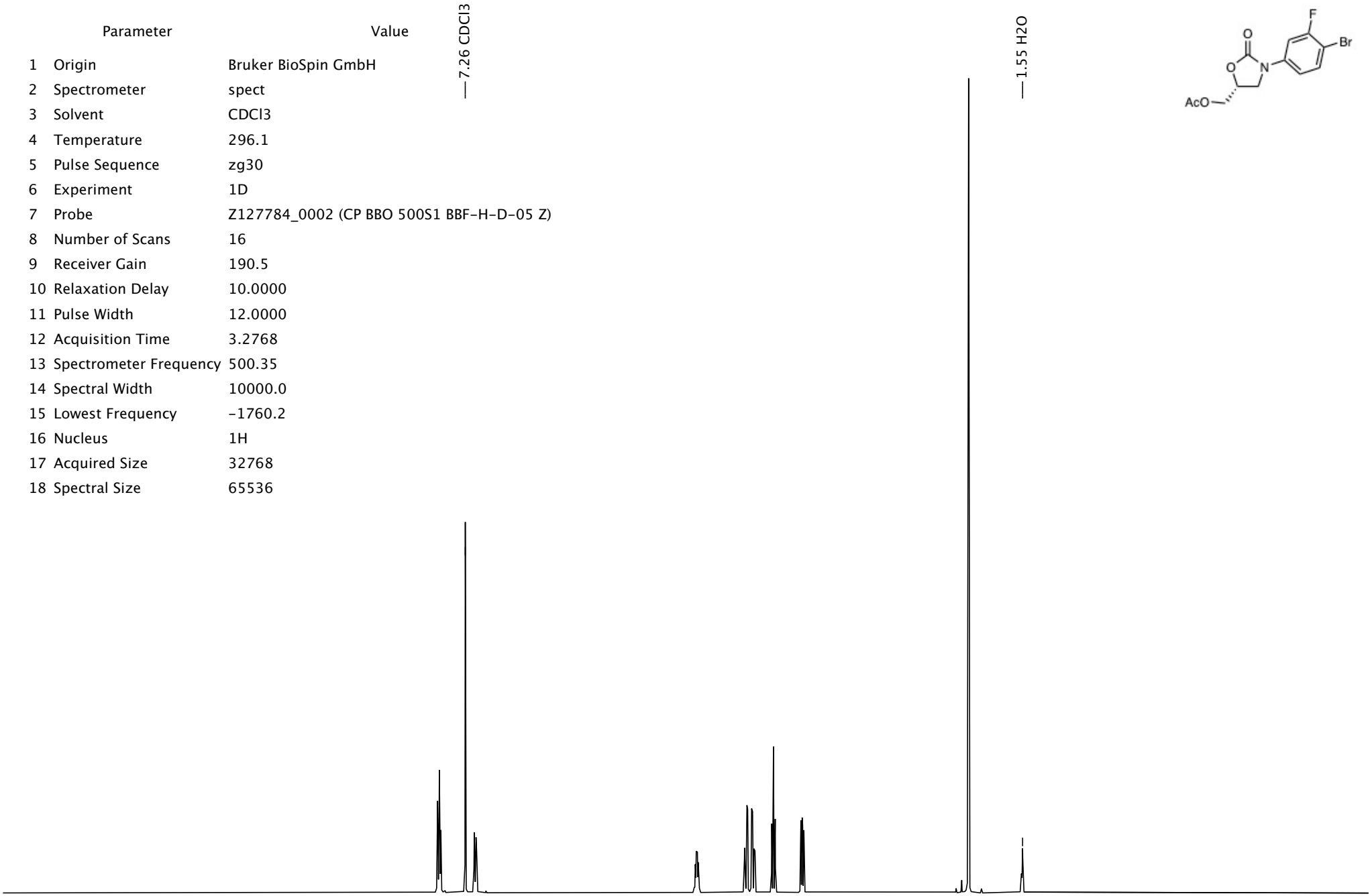
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	cosygpppqf
6	Experiment	COSY
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	4
9	Receiver Gain	61.8
10	Relaxation Delay	1.8951
11	Pulse Width	12.0000
12	Acquisition Time	0.2621
13	Spectrometer Frequency	(500.35, 500.35)
14	Spectral Width	(3906.2, 3906.2)
15	Lowest Frequency	(207.9, 207.9)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)



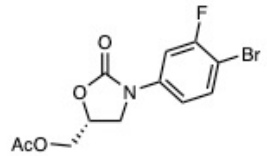
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5

f1 (ppm)

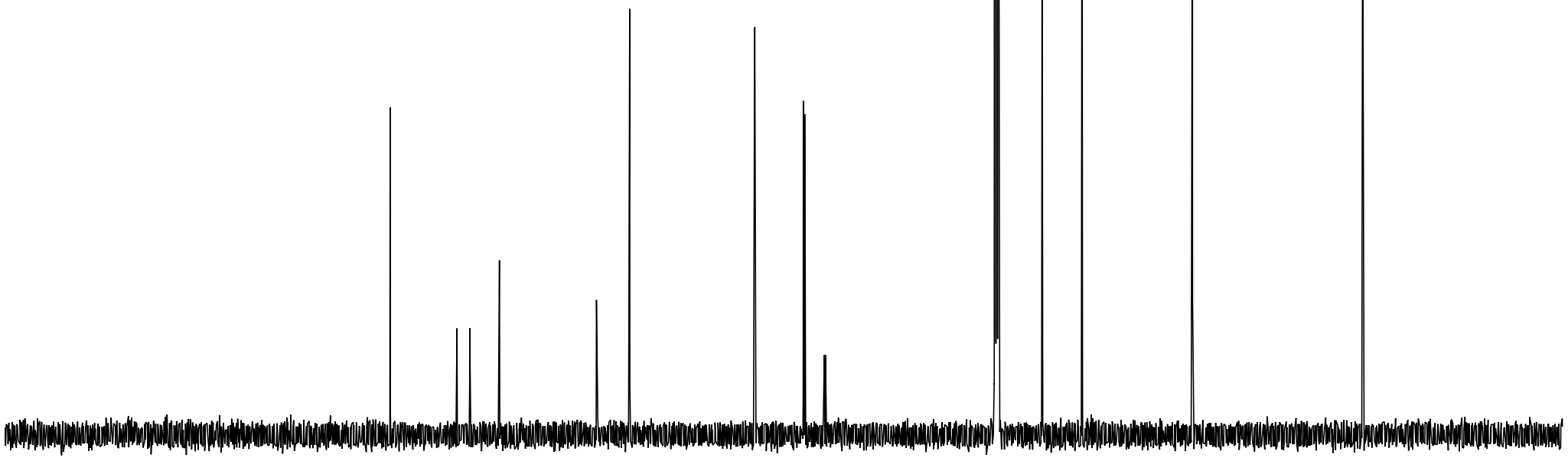
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1760.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

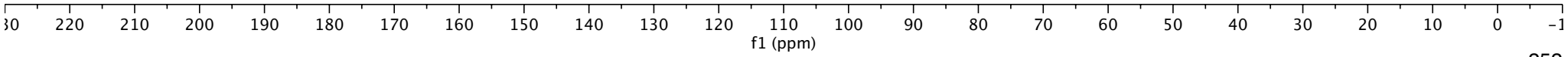


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

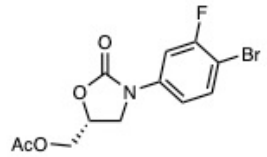


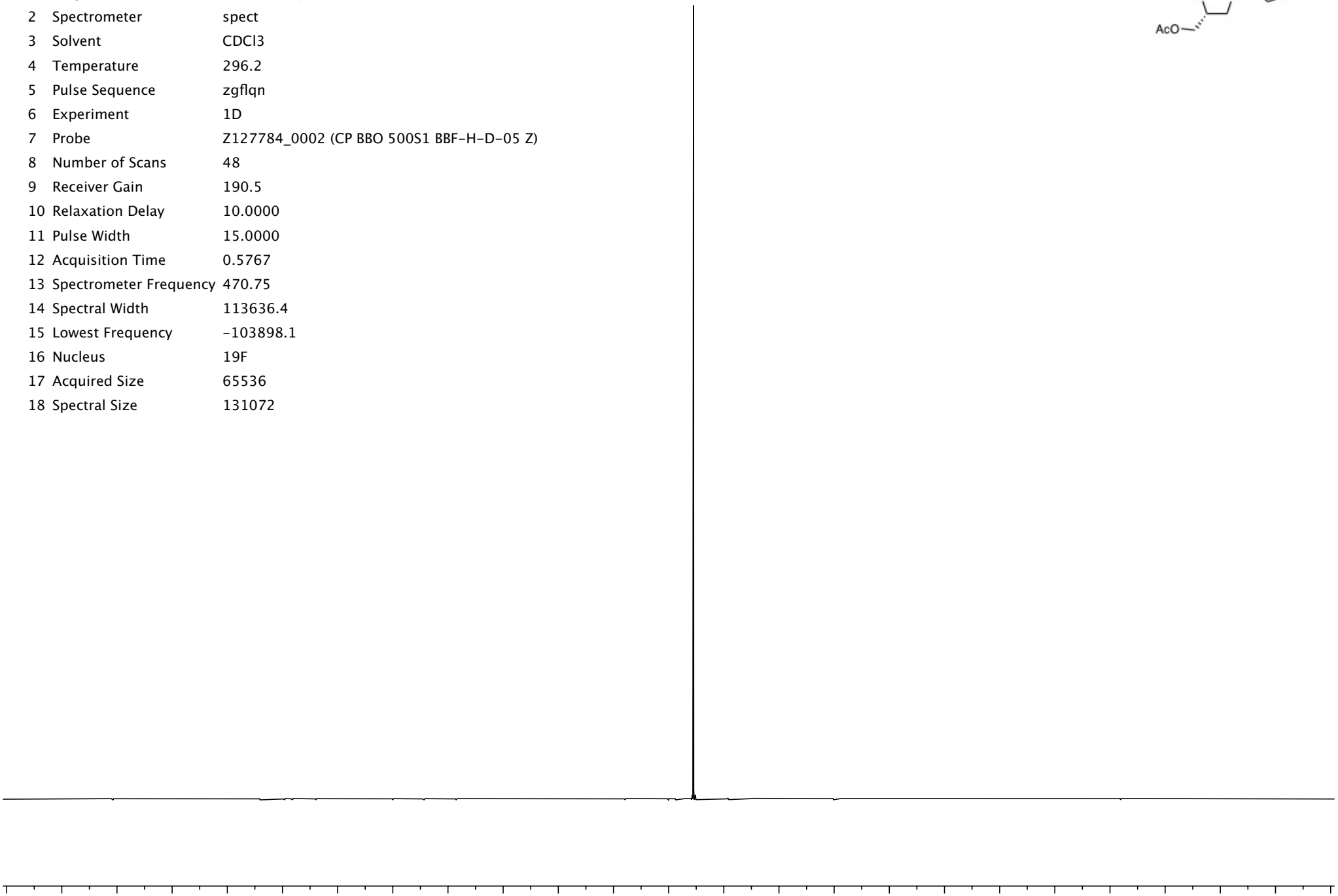
77.16 CDCl3



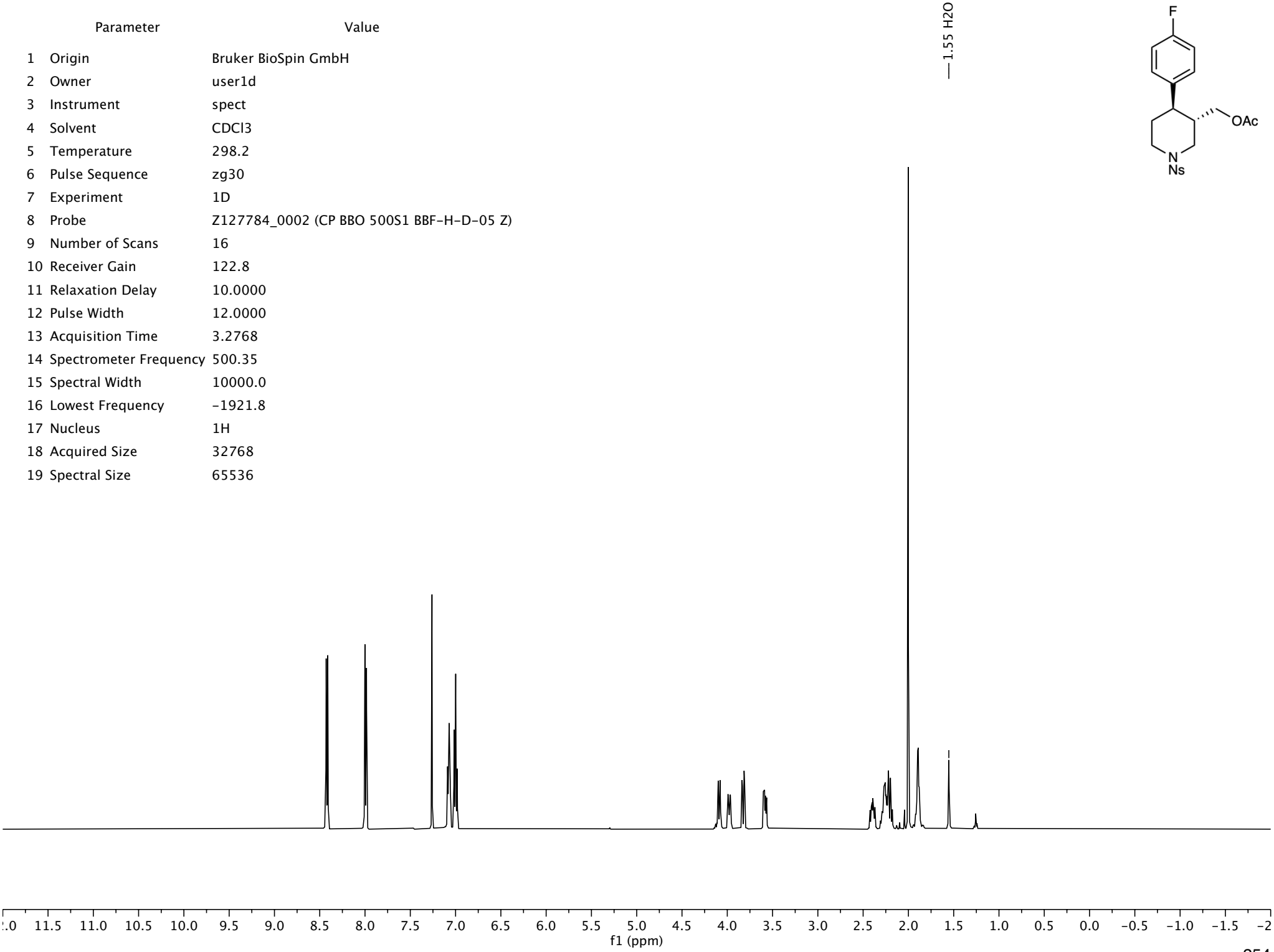


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	48
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	15.0000
12	Acquisition Time	0.5767
13	Spectrometer Frequency	470.75
14	Spectral Width	113636.4
15	Lowest Frequency	-103898.1
16	Nucleus	19F
17	Acquired Size	65536
18	Spectral Size	131072

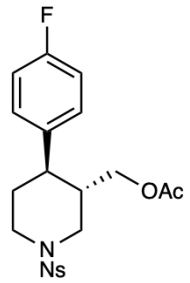




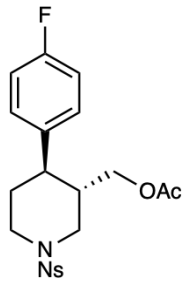
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	122.8
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1921.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

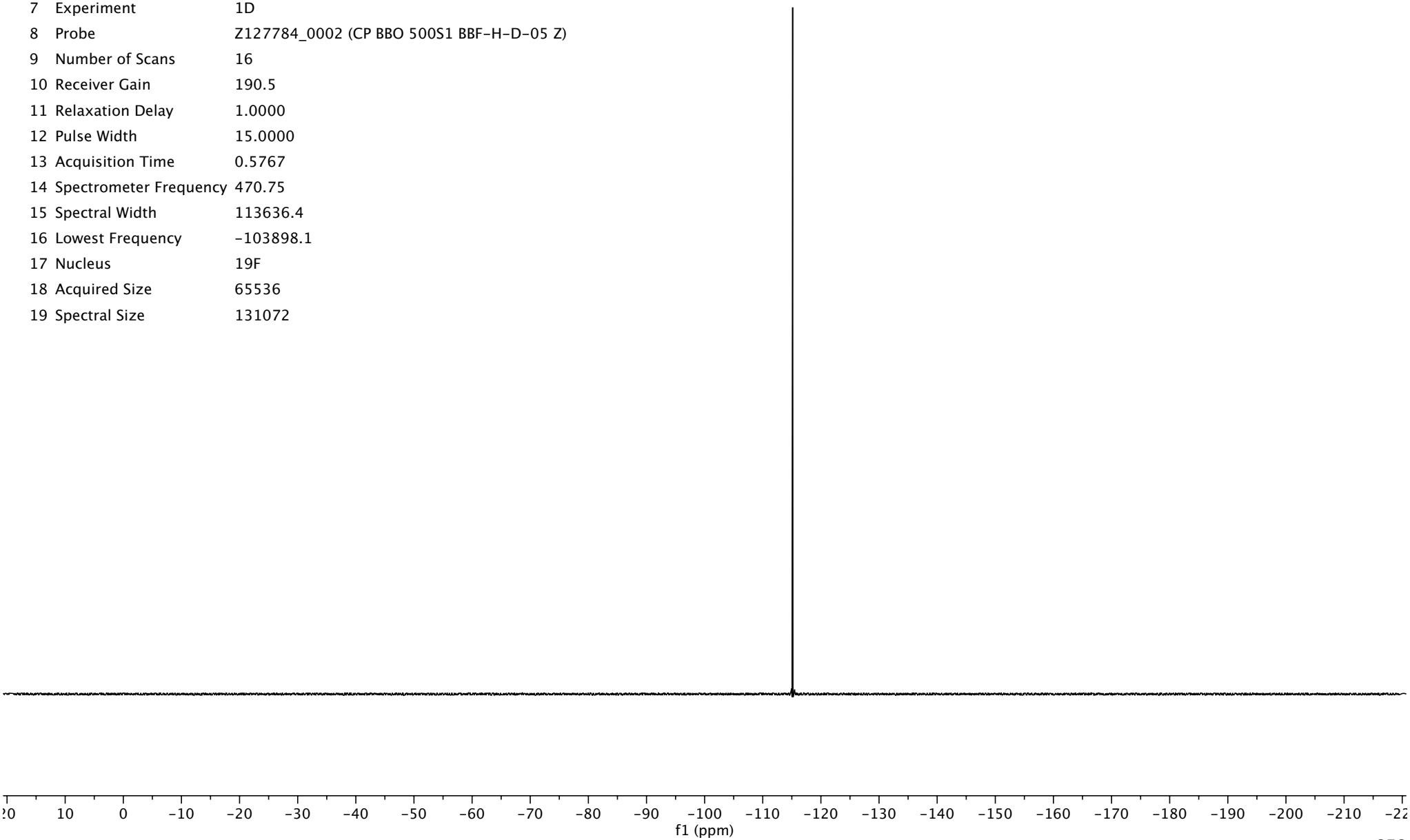


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1873.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

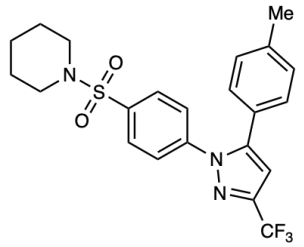


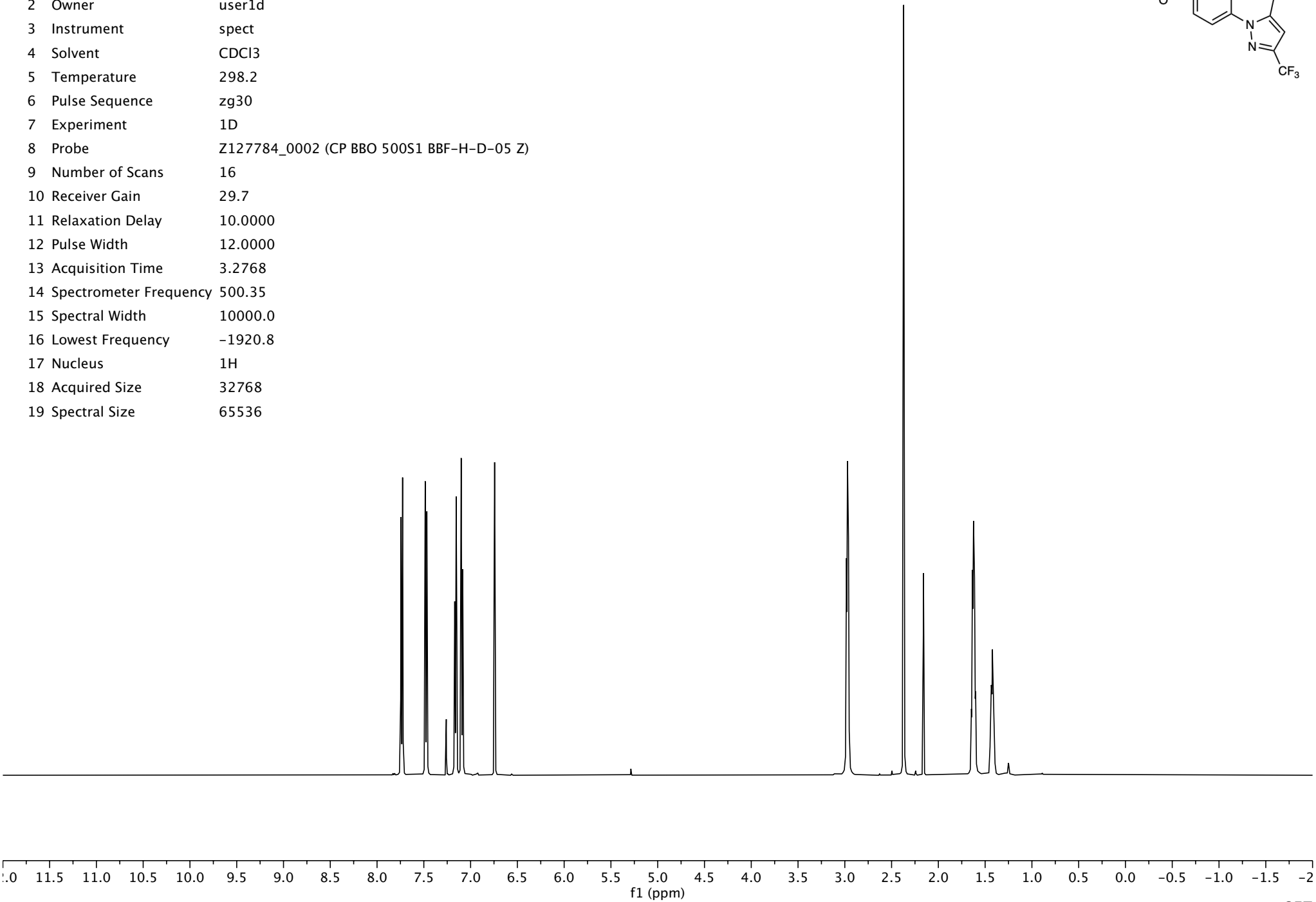
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



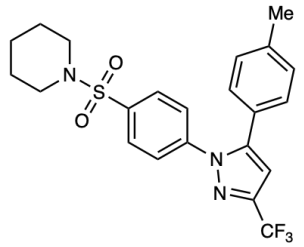


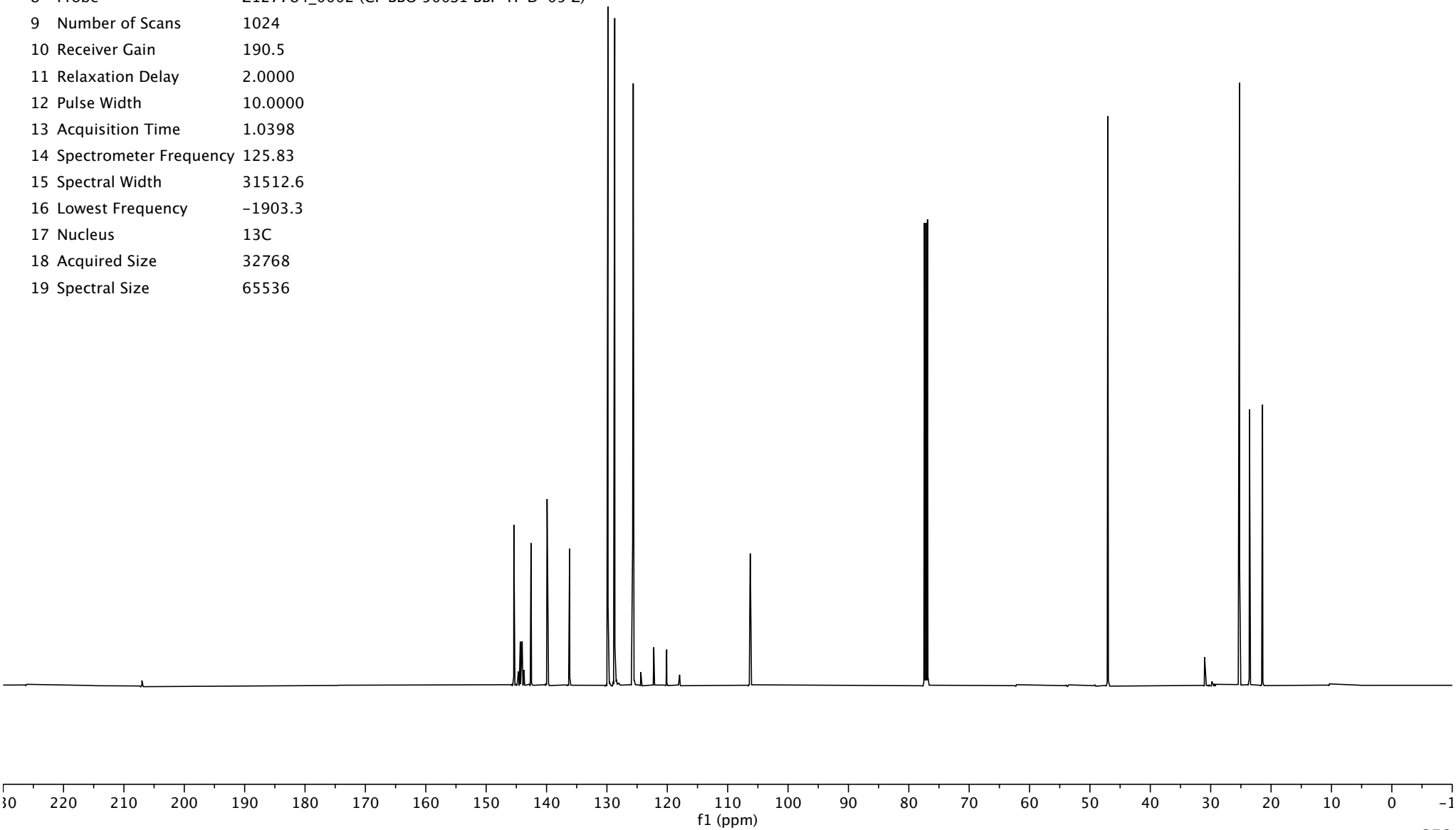
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1920.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

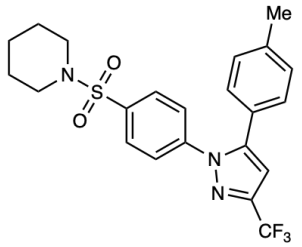




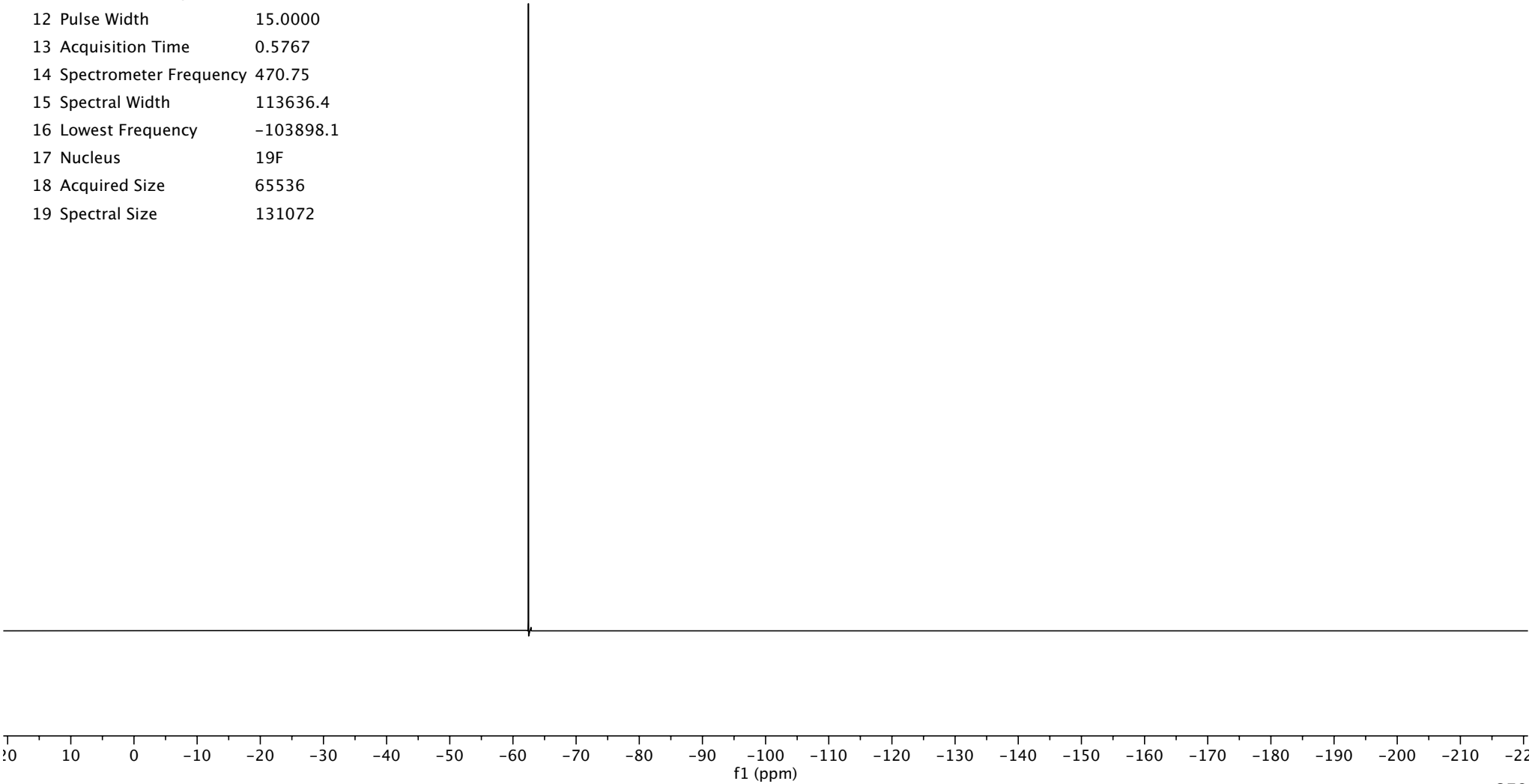
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1903.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



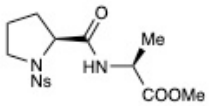


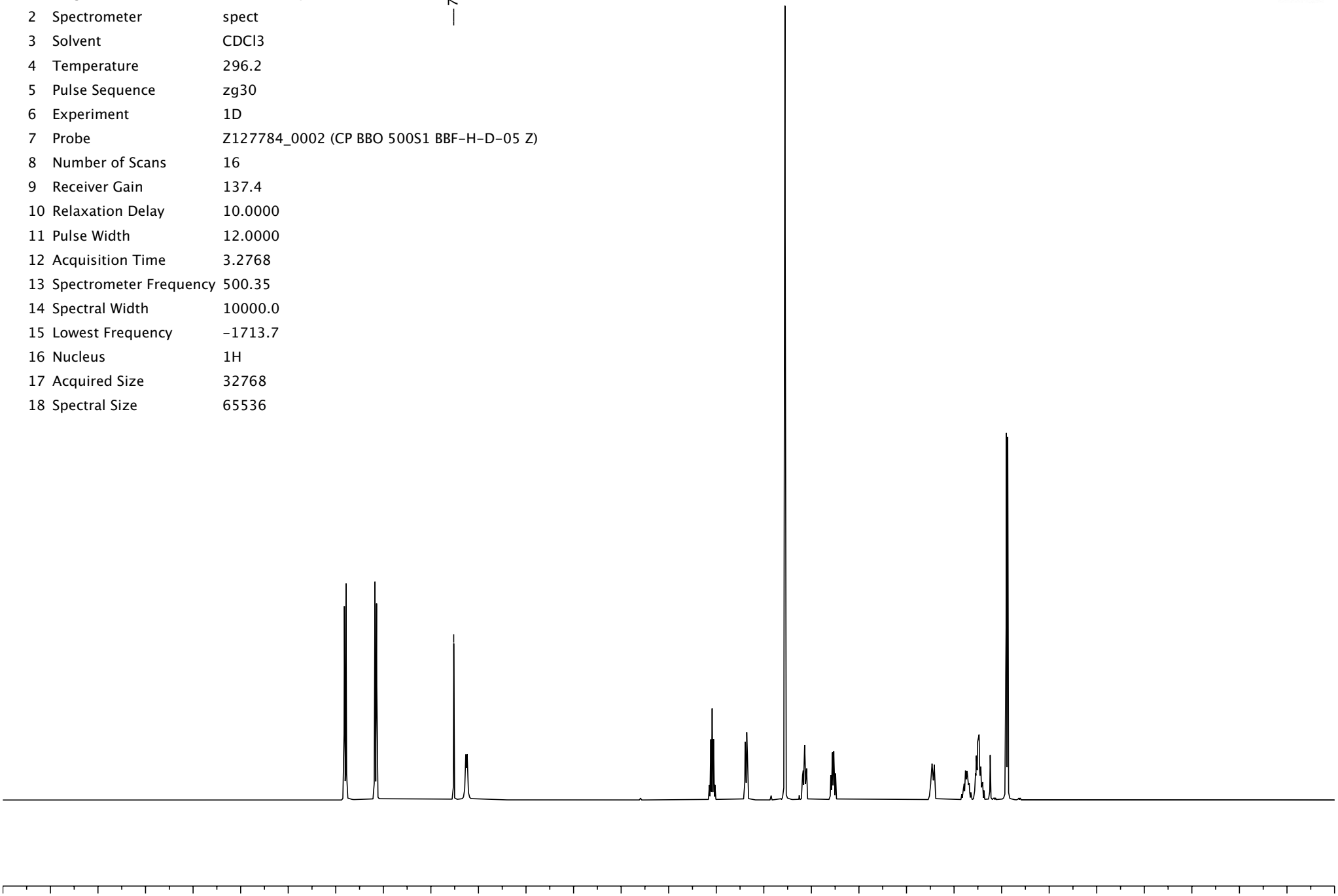


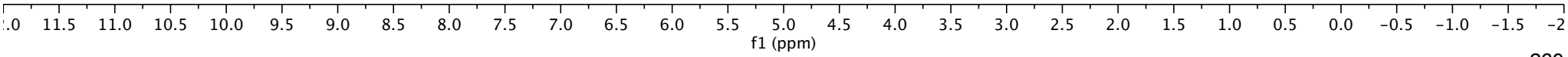
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



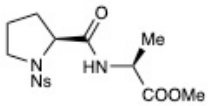
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	137.4
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1713.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



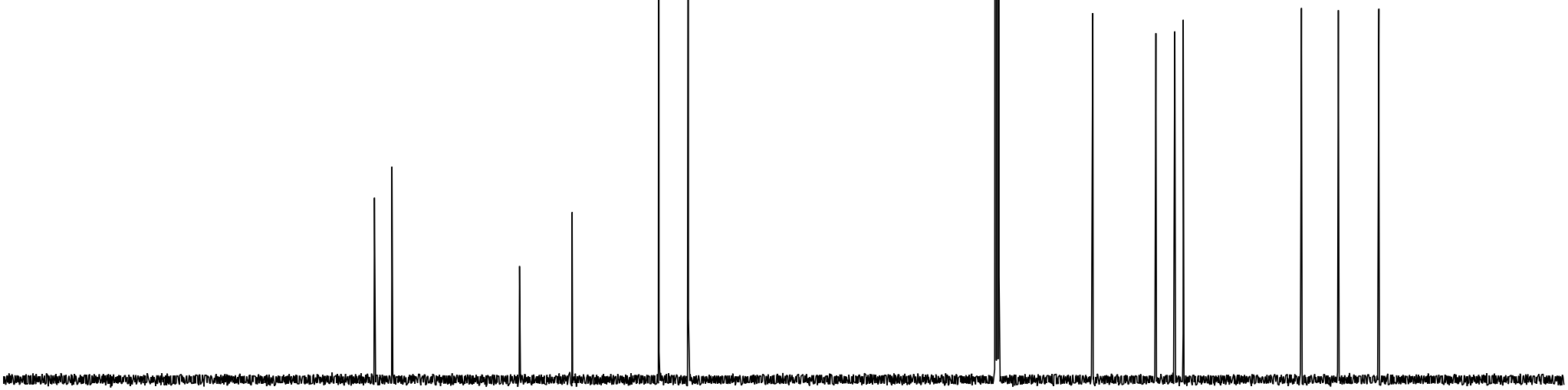


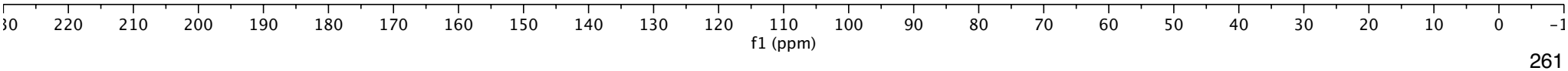


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

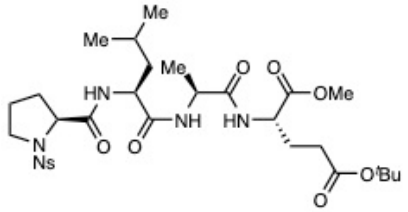


77.16 CDCl3

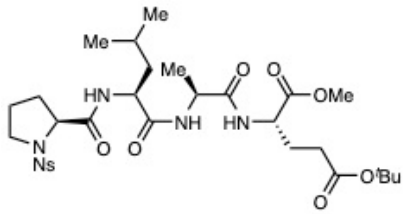




	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	168.2
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1760.2
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



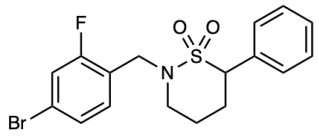
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

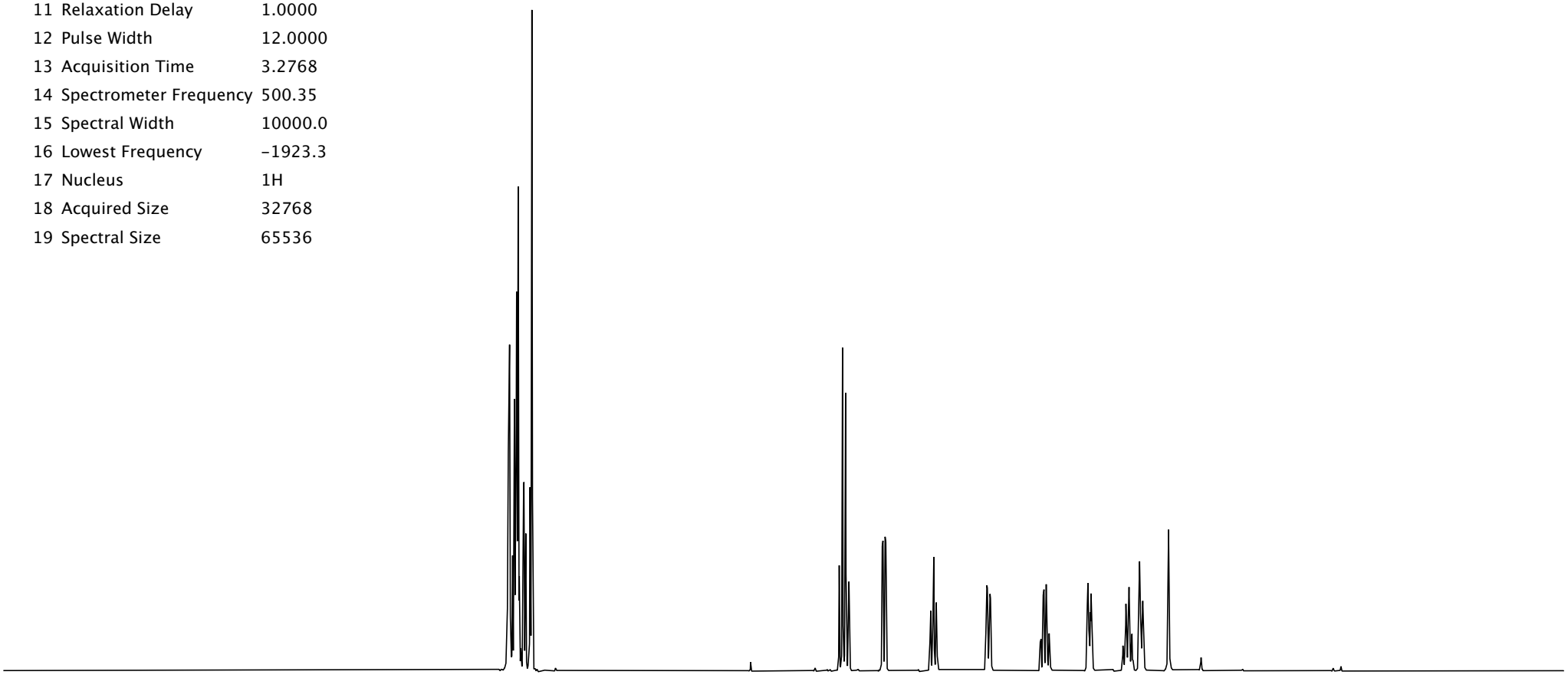


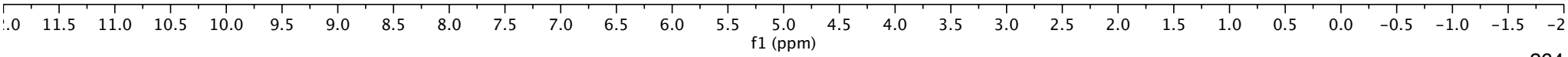
77.16 CDCl3

f1 (ppm)

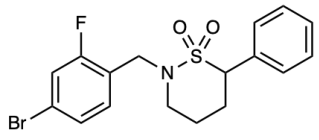
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1923.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



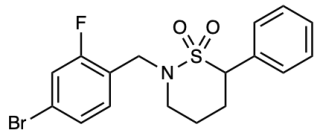


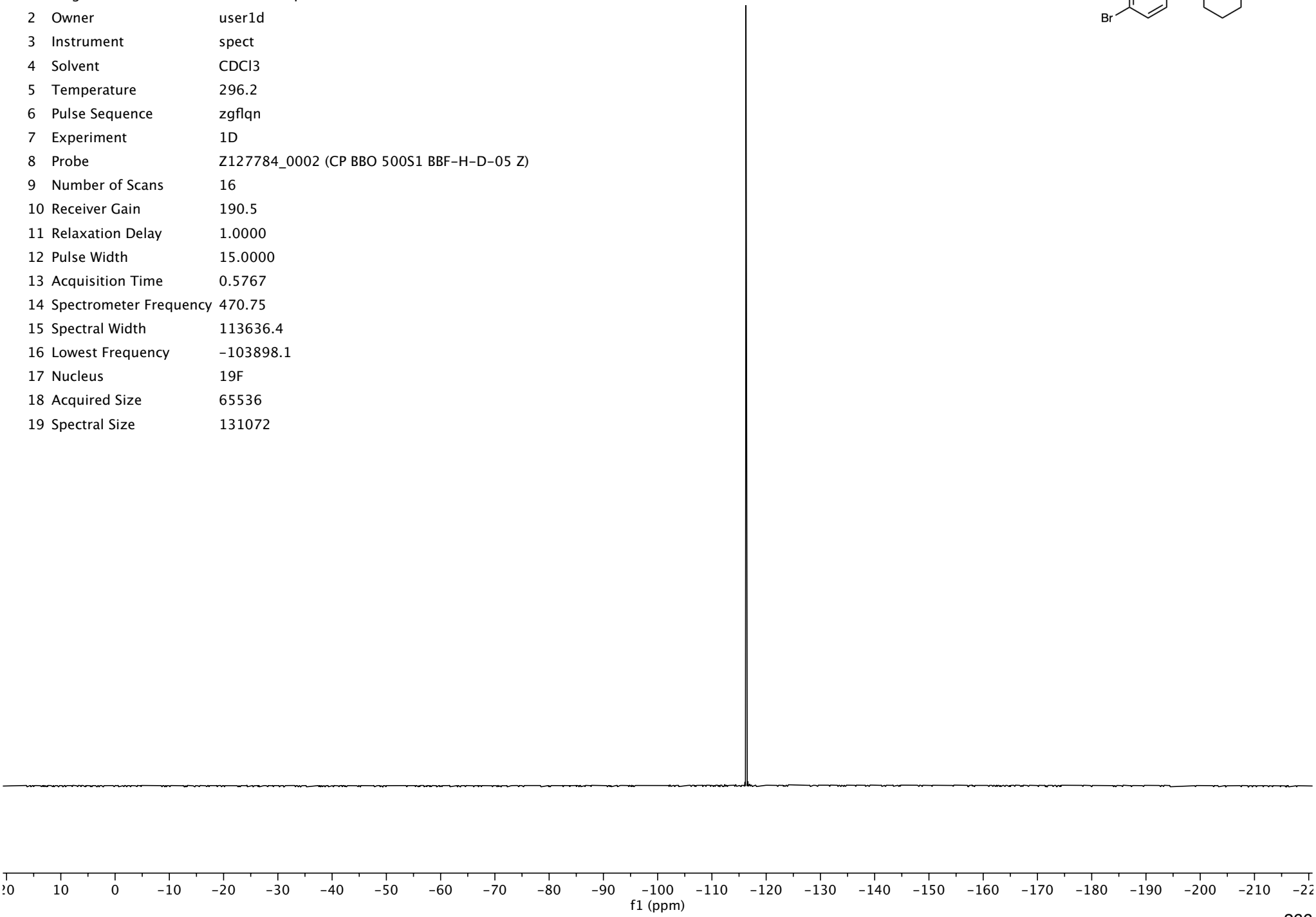


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1916.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

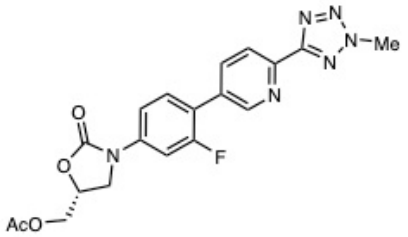


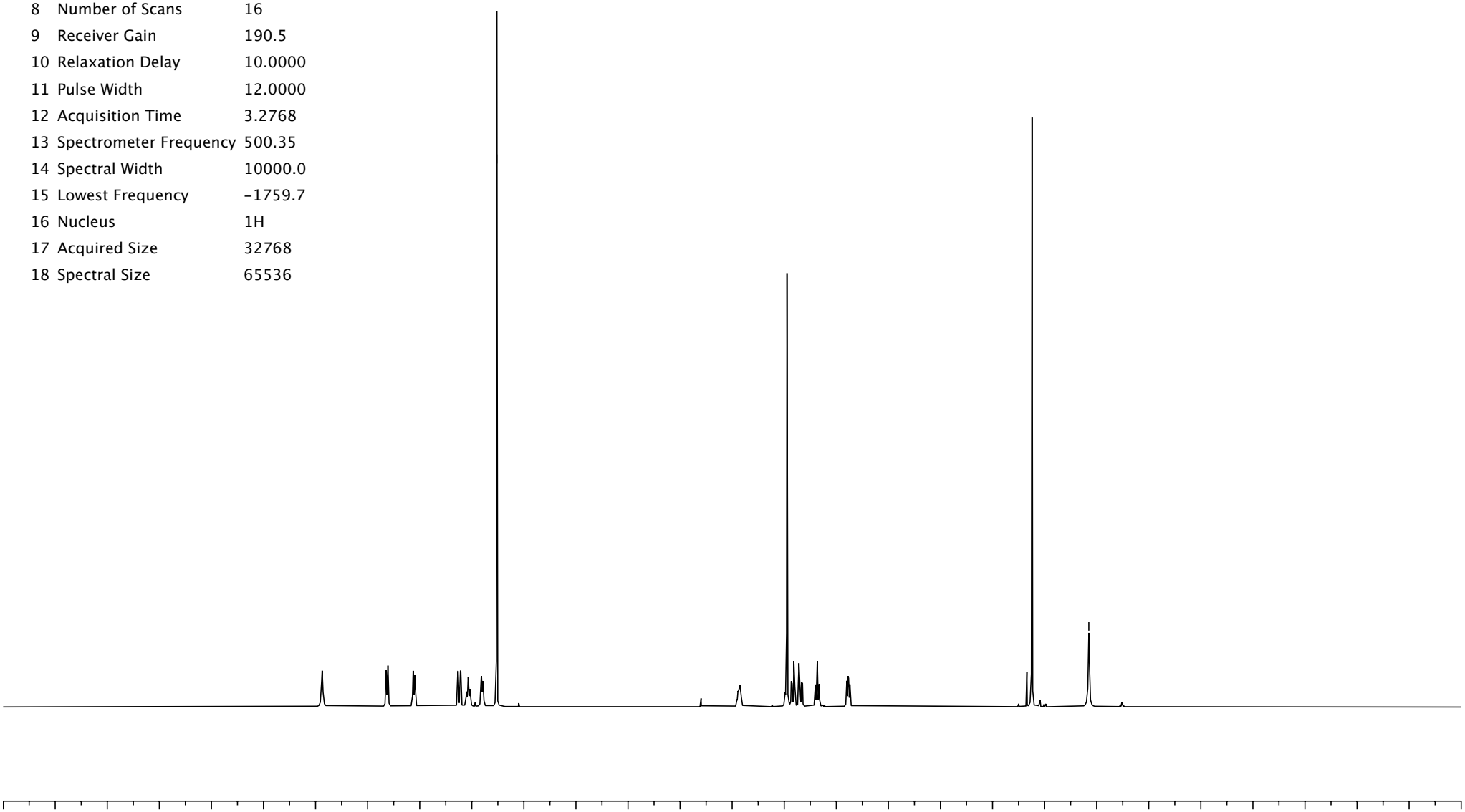
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



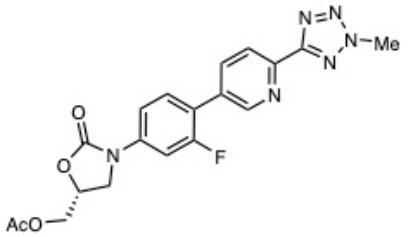


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1759.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536





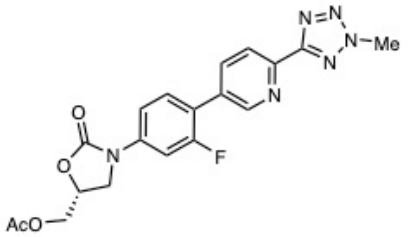
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



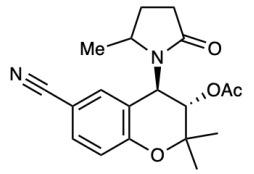
77.16 CDCl3

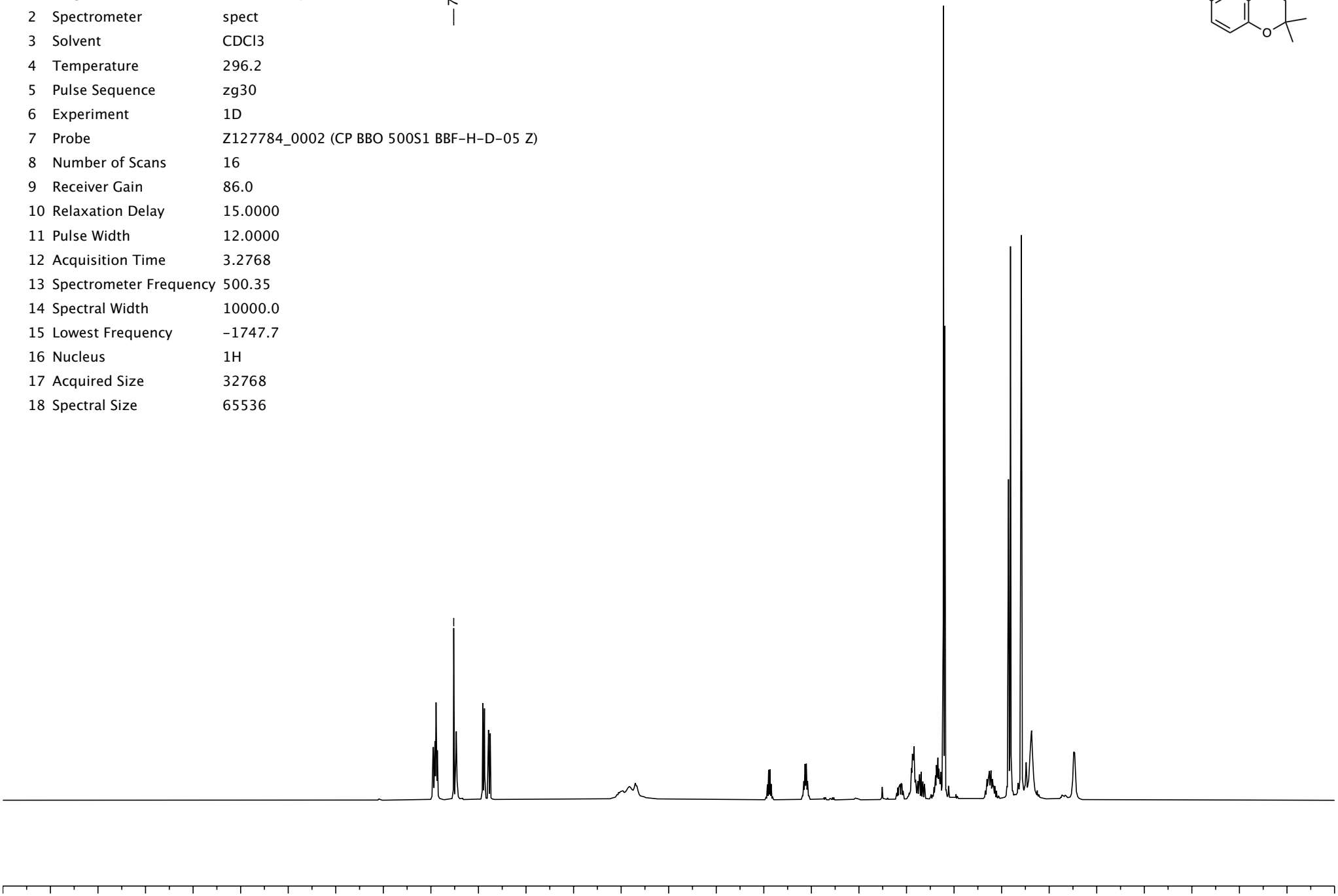
f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	80
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	15.0000
12	Acquisition Time	0.5767
13	Spectrometer Frequency	470.75
14	Spectral Width	113636.4
15	Lowest Frequency	-103898.1
16	Nucleus	19F
17	Acquired Size	65536
18	Spectral Size	131072

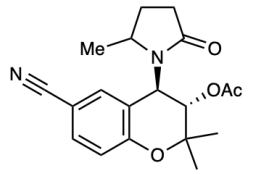


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	86.0
10	Relaxation Delay	15.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1747.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

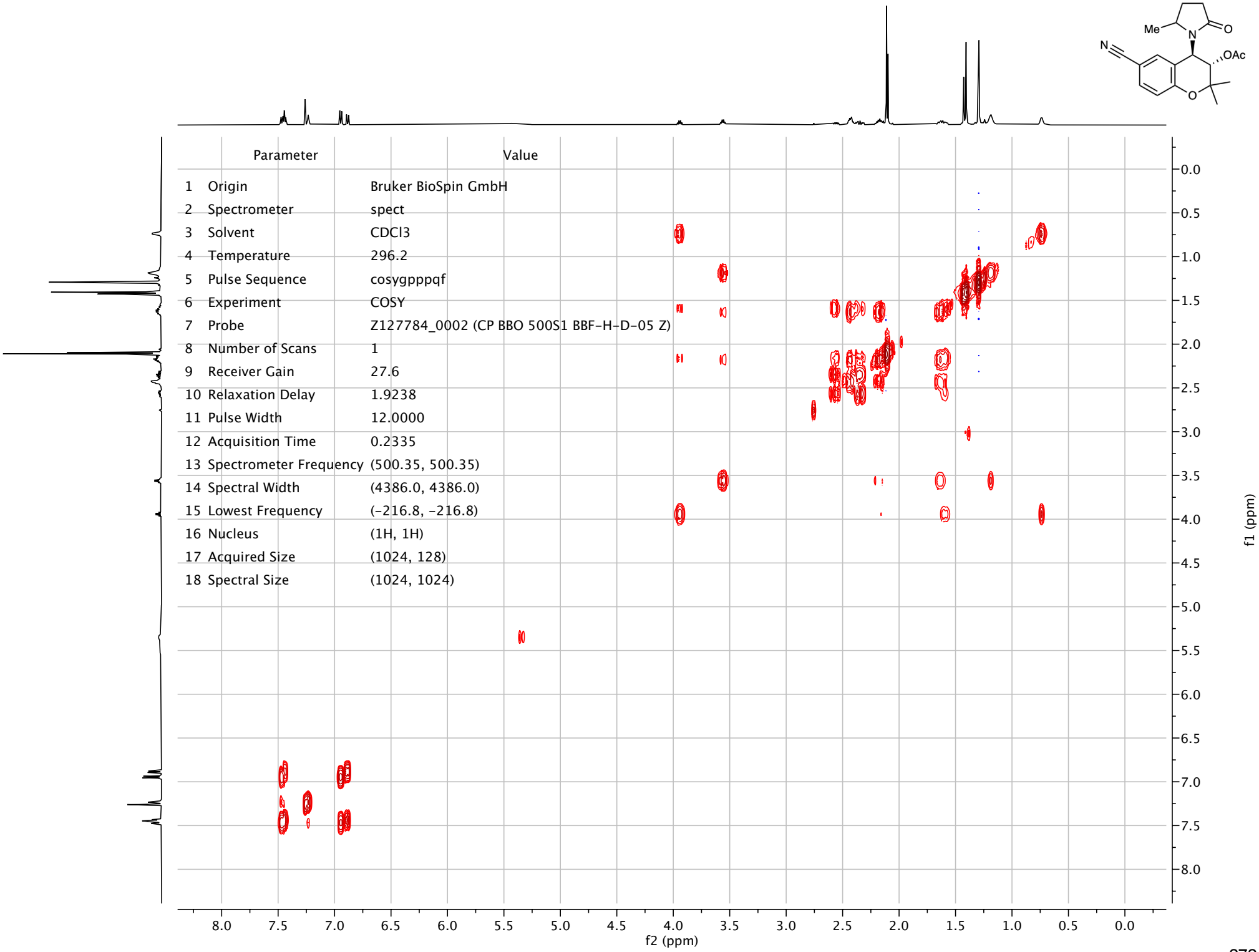




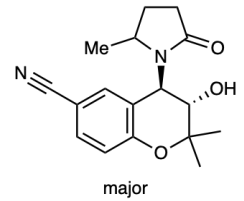
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1902.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



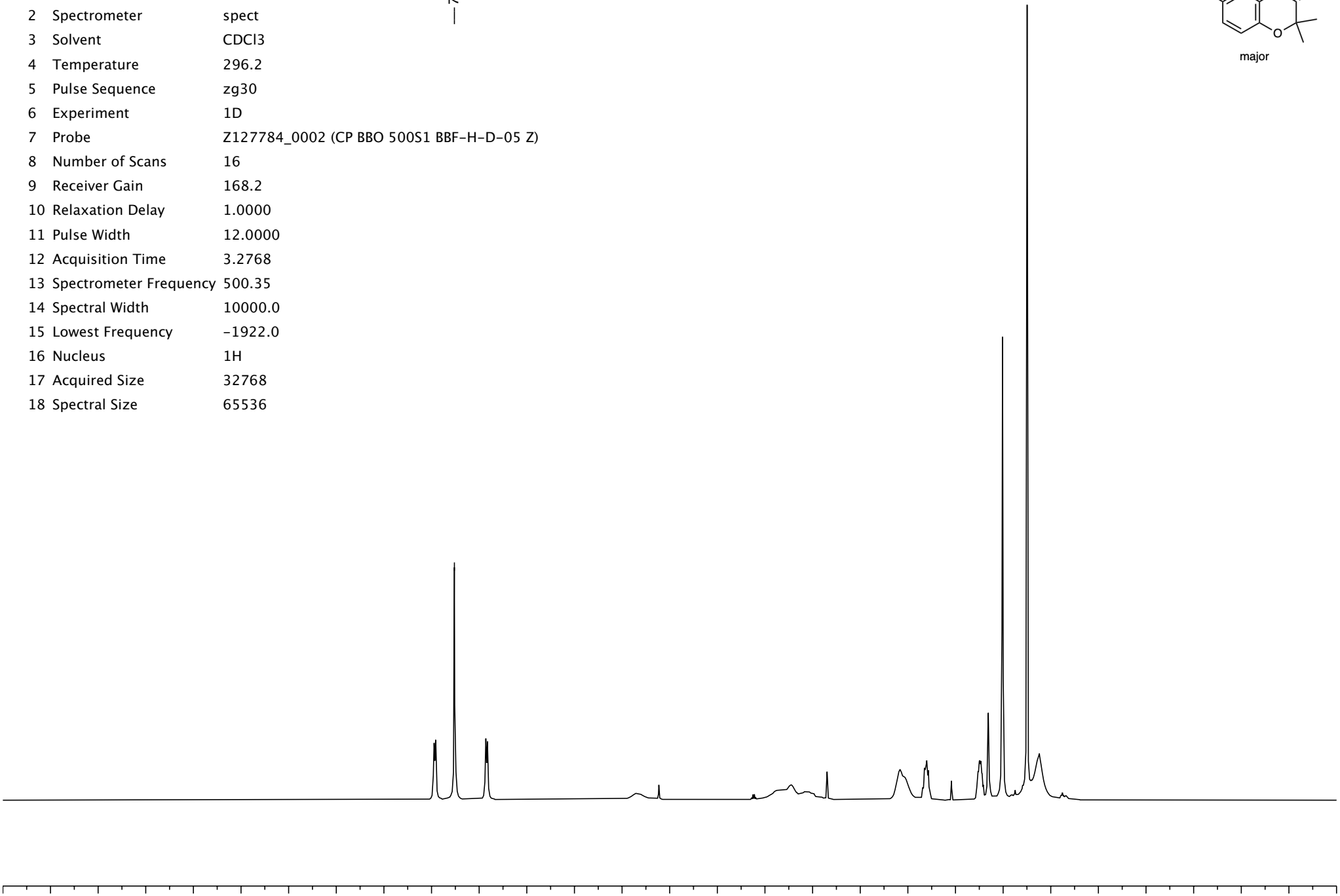
77.16 CDCl3


Me
N
O
N
OAc
O
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 296.2
5 Pulse Sequence cosygpppqf
6 Experiment COSY
7 Probe Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8 Number of Scans 1
9 Receiver Gain 27.6
10 Relaxation Delay 1.9238
11 Pulse Width 12.0000
12 Acquisition Time 0.2335
13 Spectrometer Frequency (500.35, 500.35)
14 Spectral Width (4386.0, 4386.0)
15 Lowest Frequency (-216.8, -216.8)
16 Nucleus (1H, 1H)
17 Acquired Size (1024, 128)
18 Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)

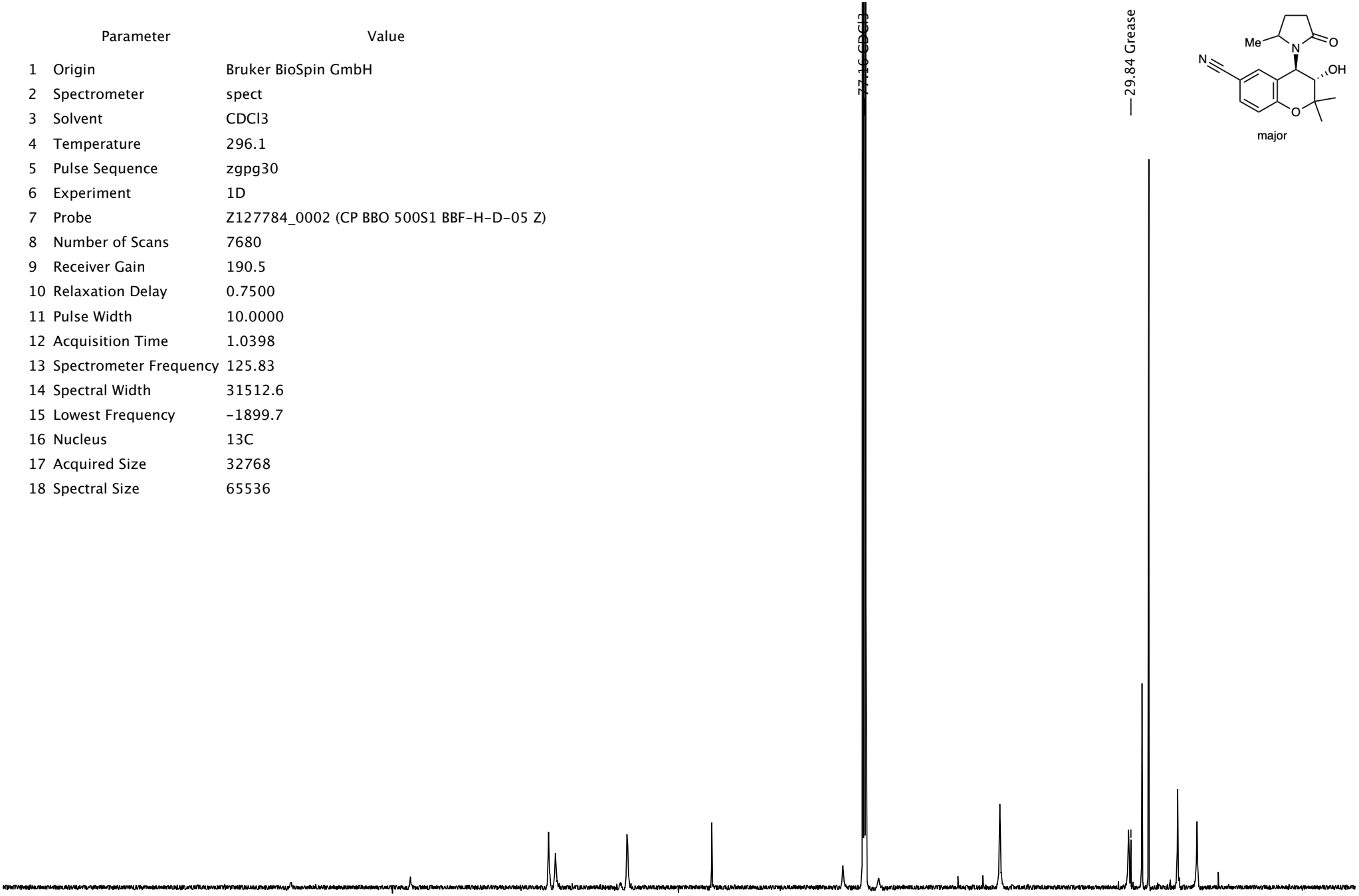
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	168.2
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.0
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



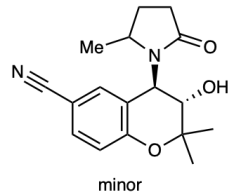
major



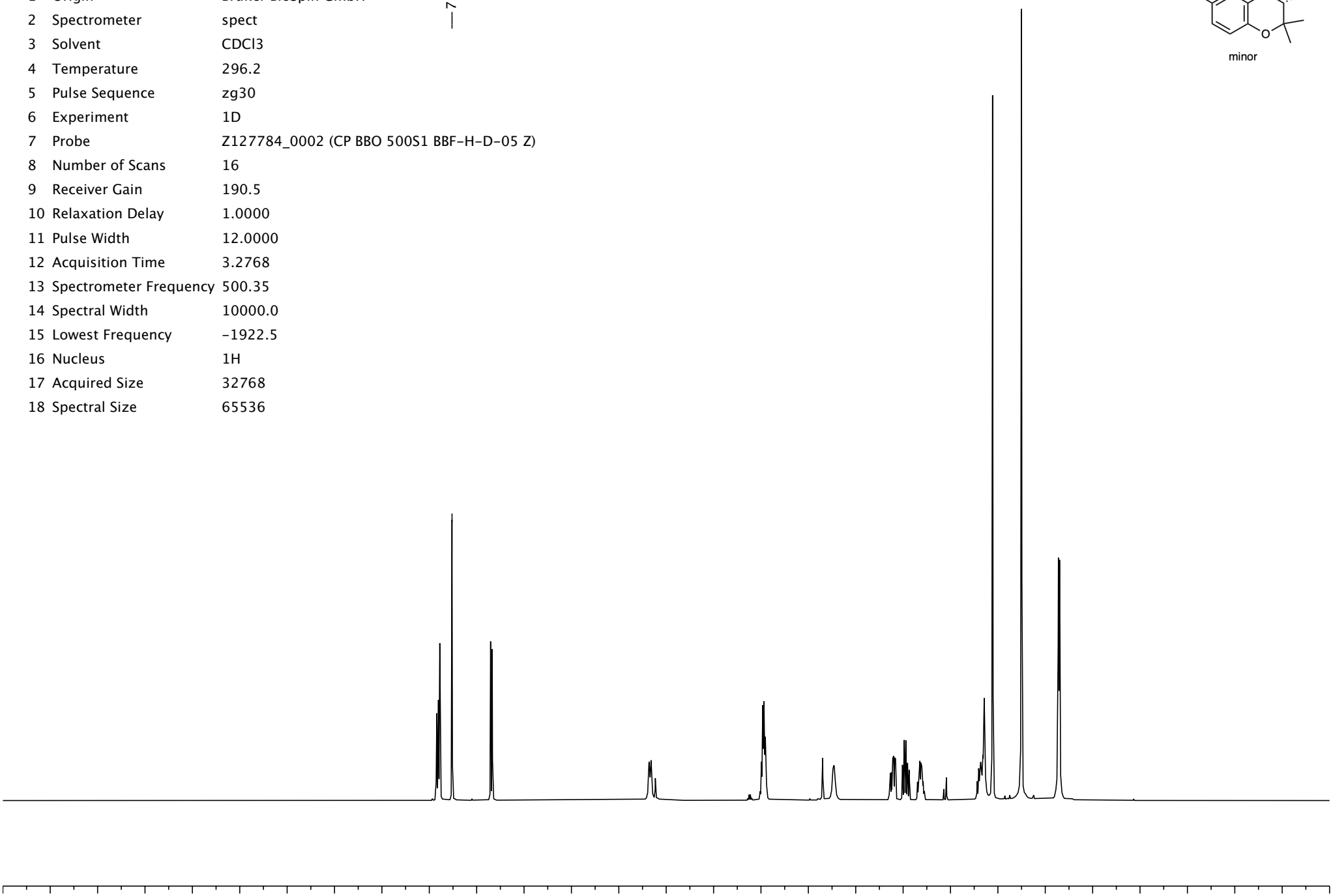
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	7680
9	Receiver Gain	190.5
10	Relaxation Delay	0.7500
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.7
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

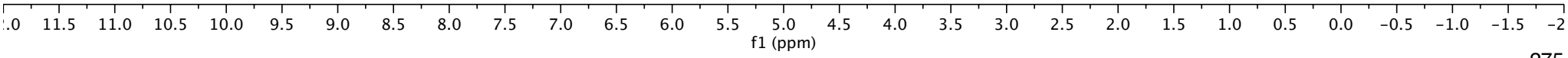


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



minor

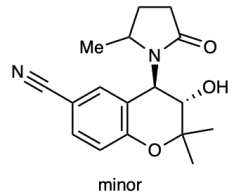




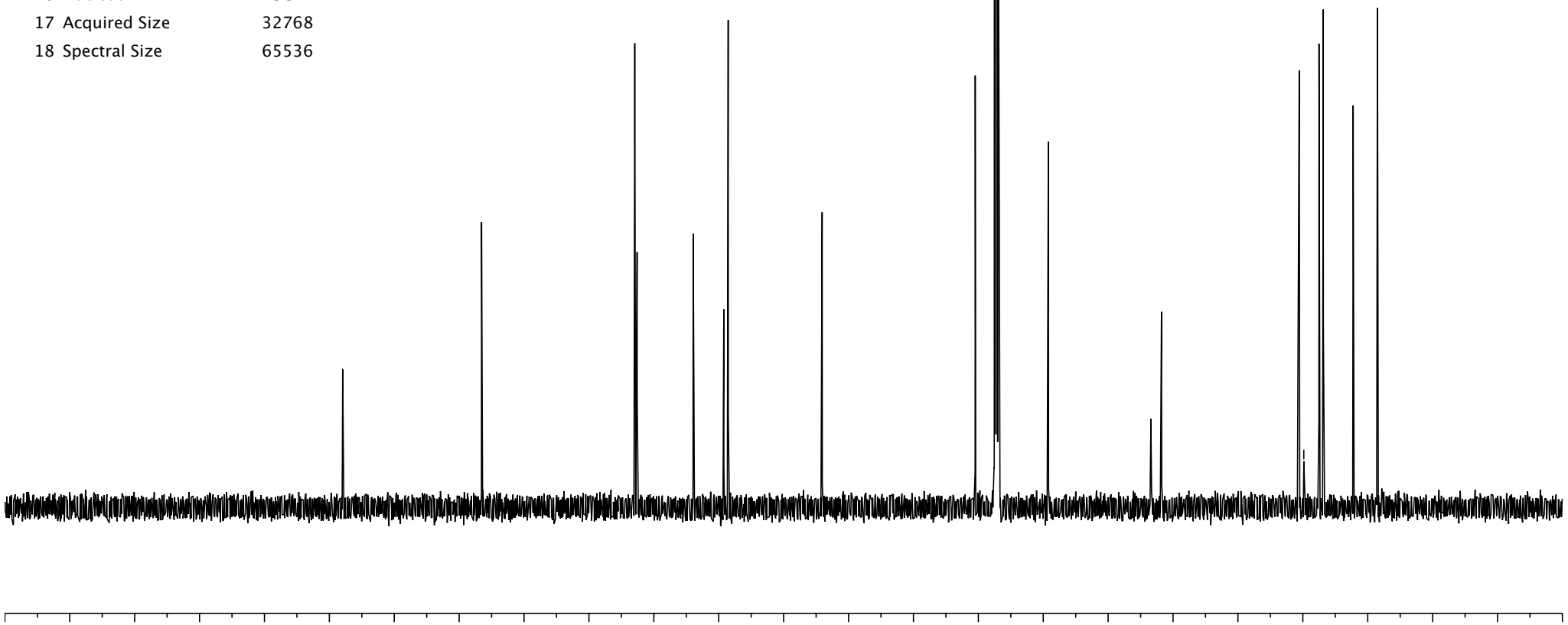
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

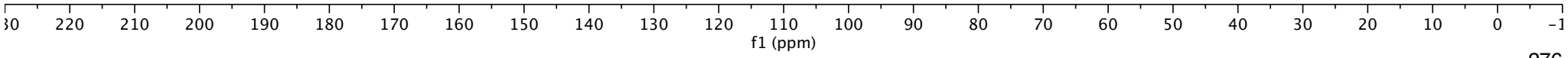
77.16 CDCl3

29.85 Grease

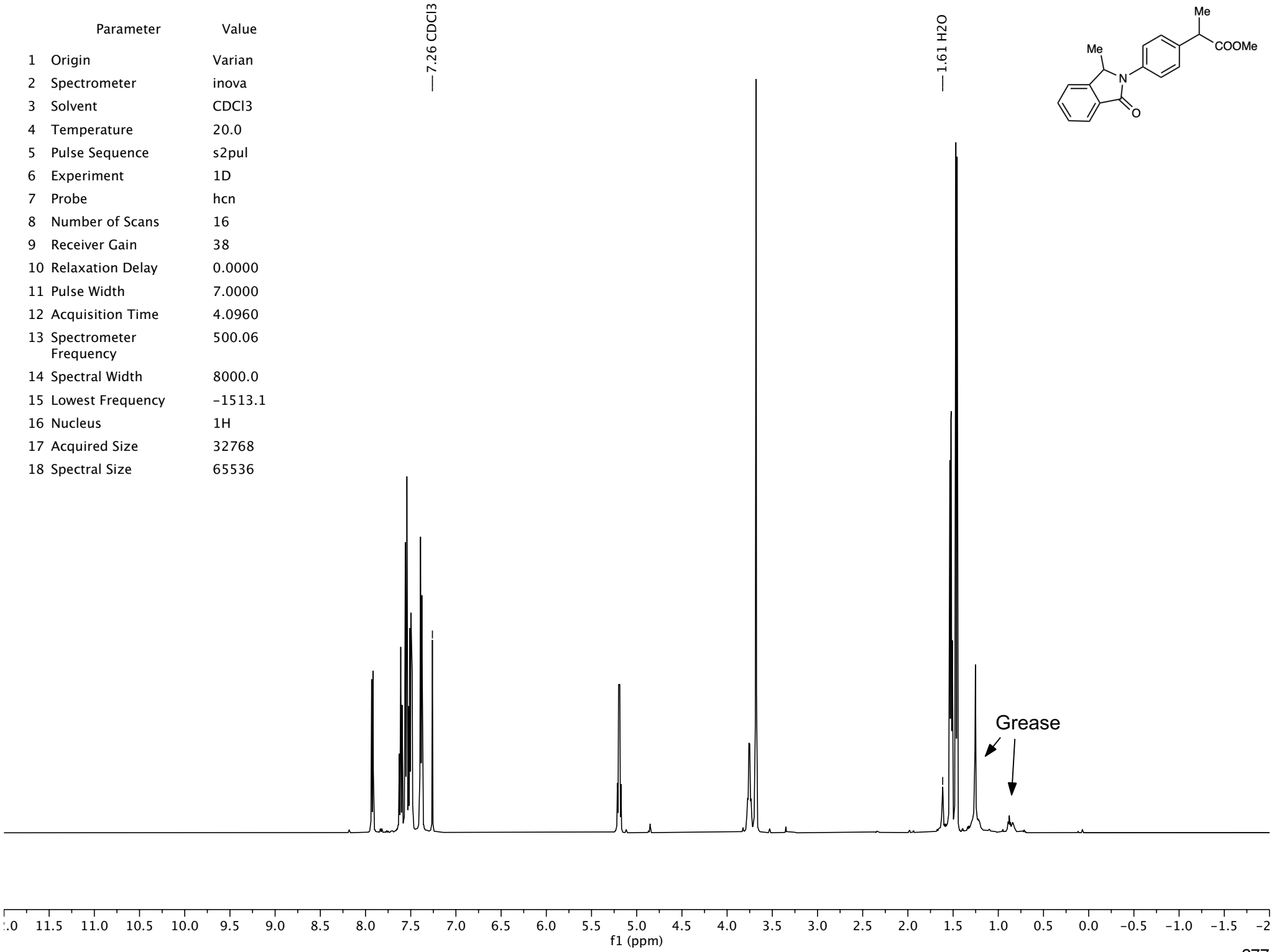


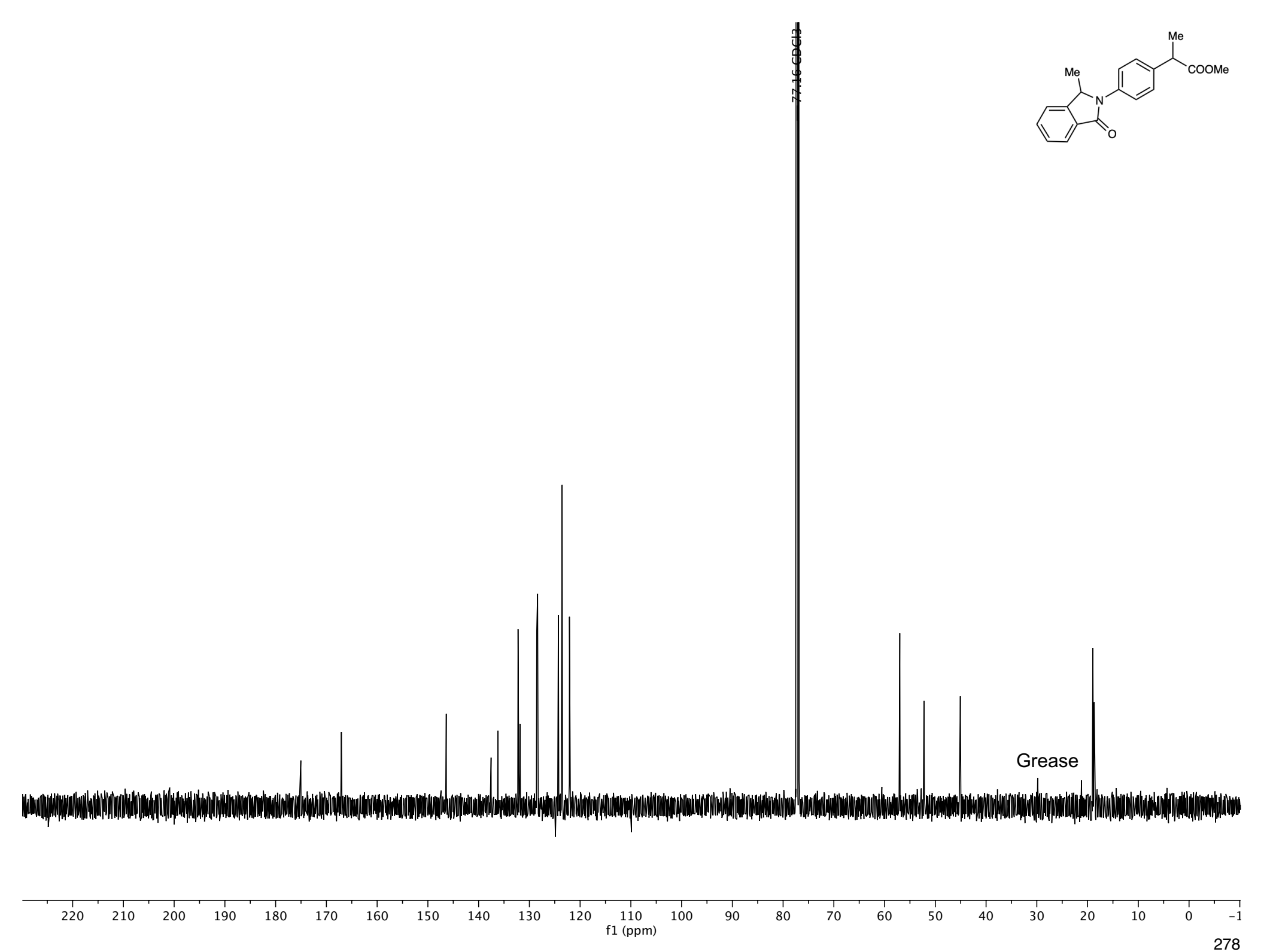
minor



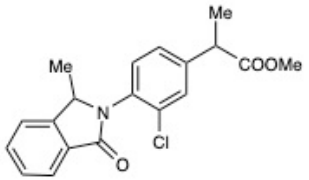


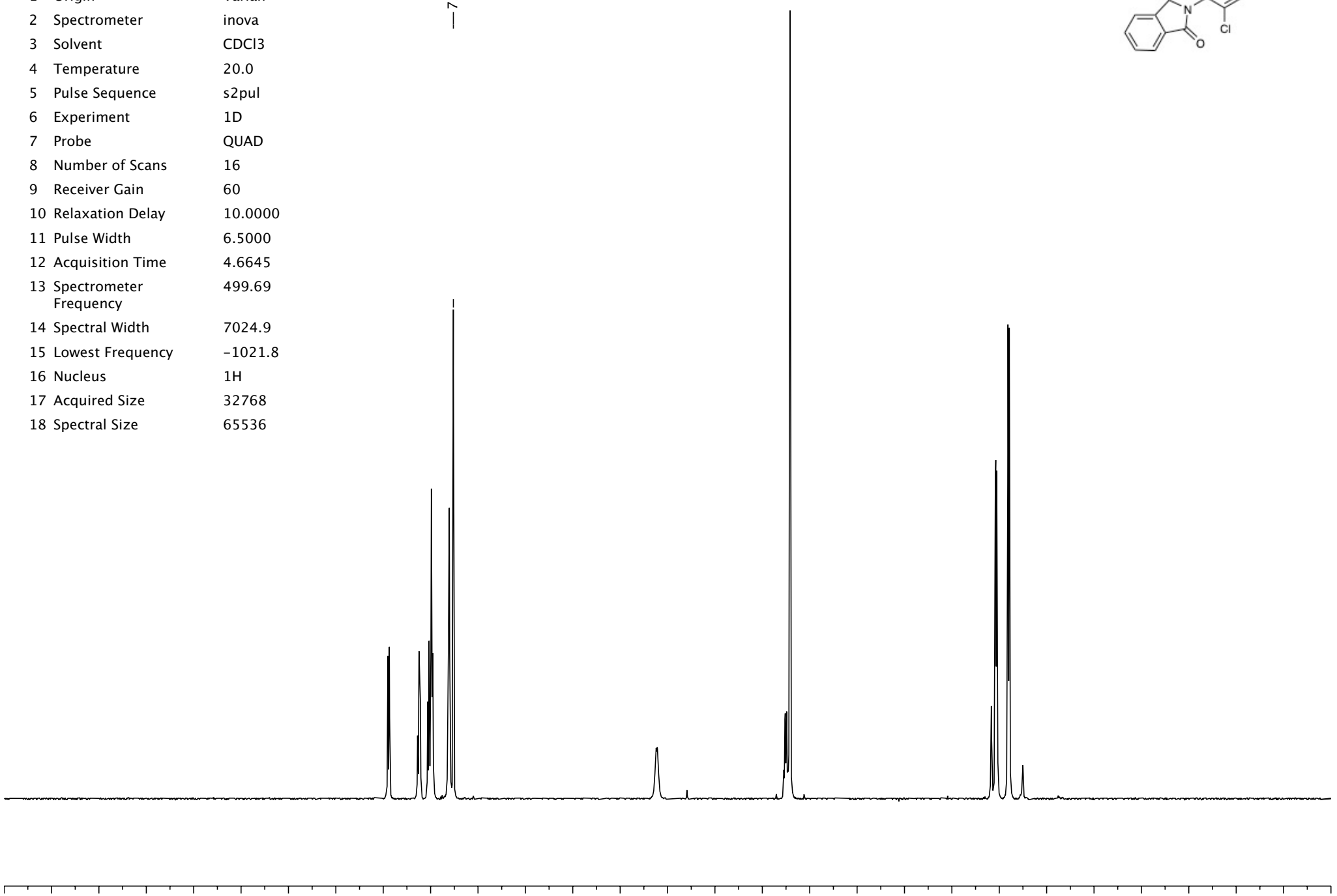
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



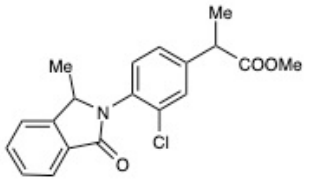

77.16 CDCl3
Me
Me
N
O
COOMe
Grease
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

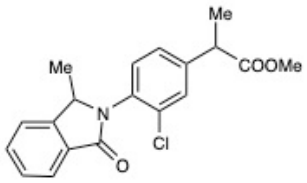
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-1021.8
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



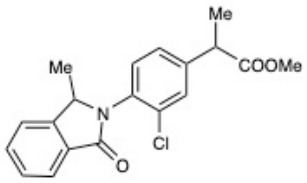


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	2560
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



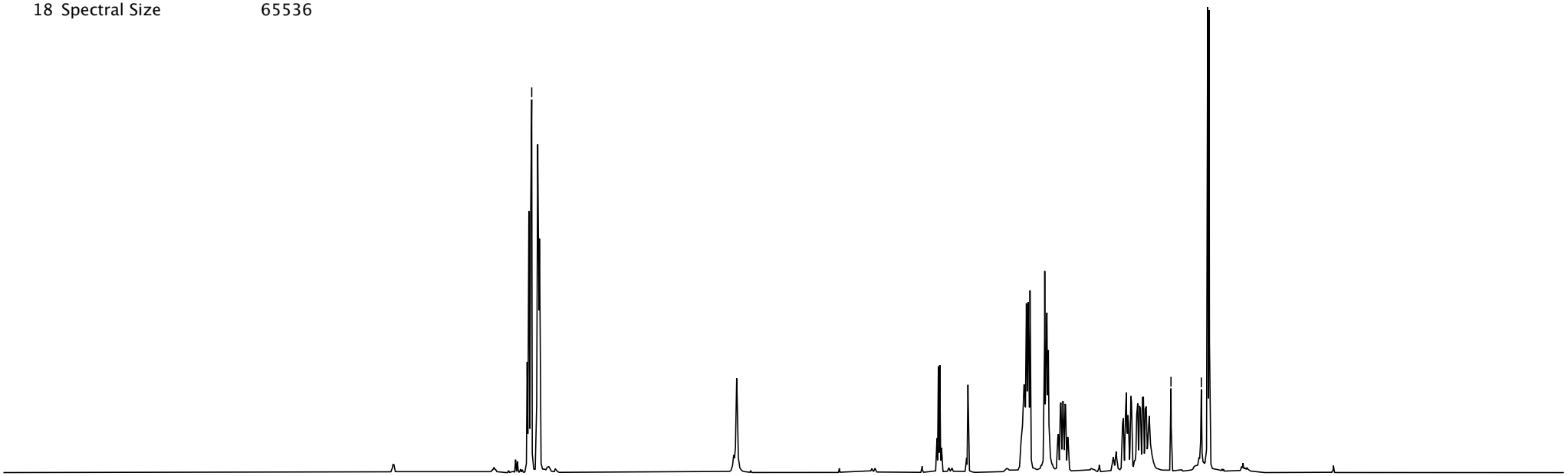


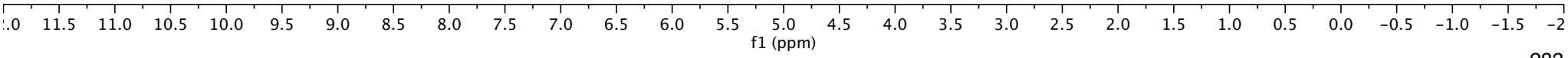
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	hsqcedetgp
6	Experiment	HSQC-EDITED
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	2
9	Receiver Gain	190.5
10	Relaxation Delay	1.5000
11	Pulse Width	12.0000
12	Acquisition Time	0.1157
13	Spectrometer Frequency	(500.35, 125.82)
14	Spectral Width	(4424.8, 20746.9)
15	Lowest Frequency	(-49.4, -937.5)
16	Nucleus	(1H, 13C)
17	Acquired Size	(512, 256)
18	Spectral Size	(512, 512)



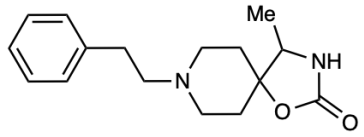
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	hmbcgplpndqf
6	Experiment	HMBC
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	4
9	Receiver Gain	190.5
10	Relaxation Delay	1.5000
11	Pulse Width	12.0000
12	Acquisition Time	0.1157
13	Spectrometer Frequency	(500.35, 125.83)
14	Spectral Width	(4424.8, 27624.3)
15	Lowest Frequency	(-49.4, -1230.8)
16	Nucleus	(1H, 13C)
17	Acquired Size	(512, 128)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	107.0
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

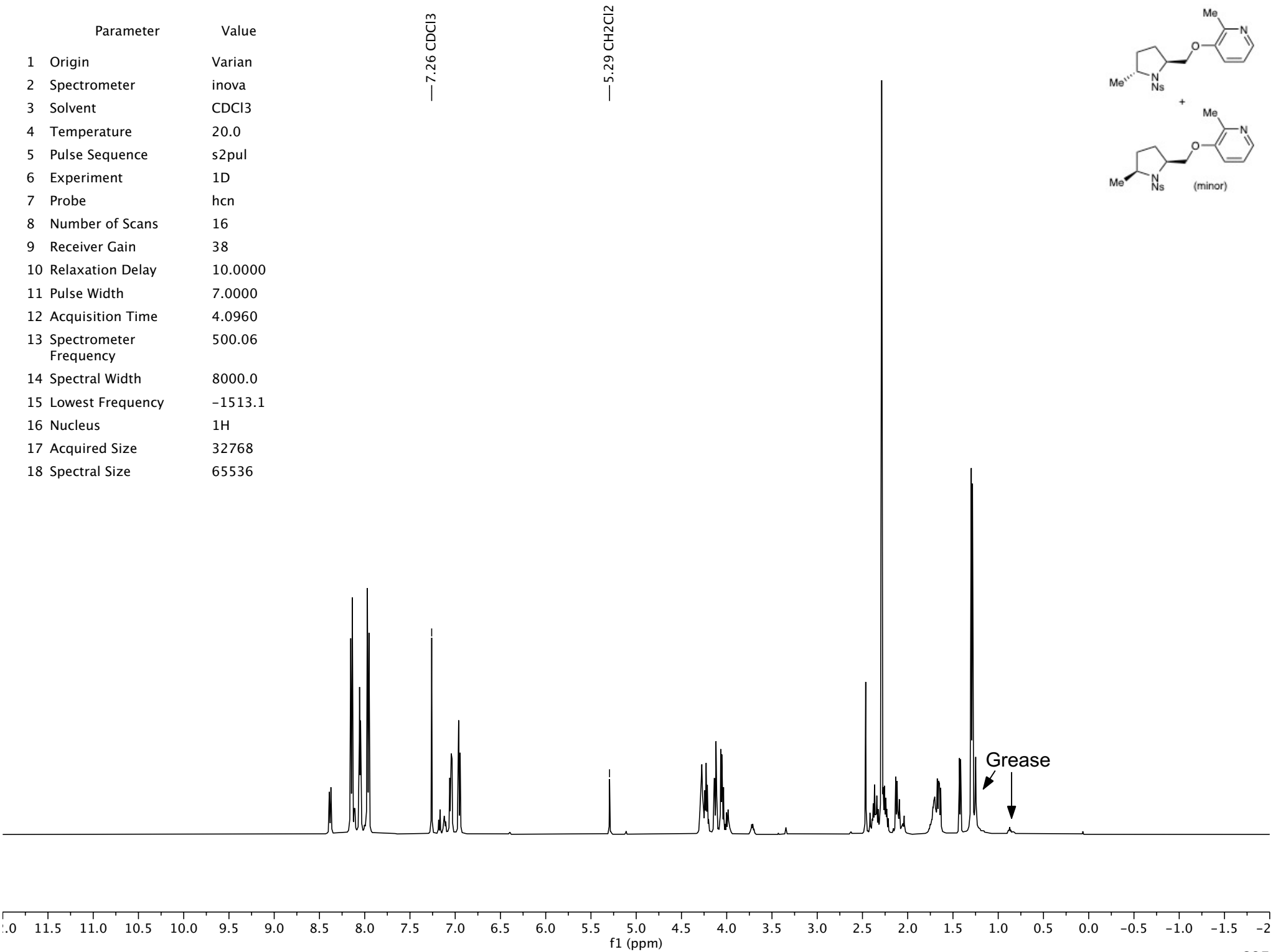




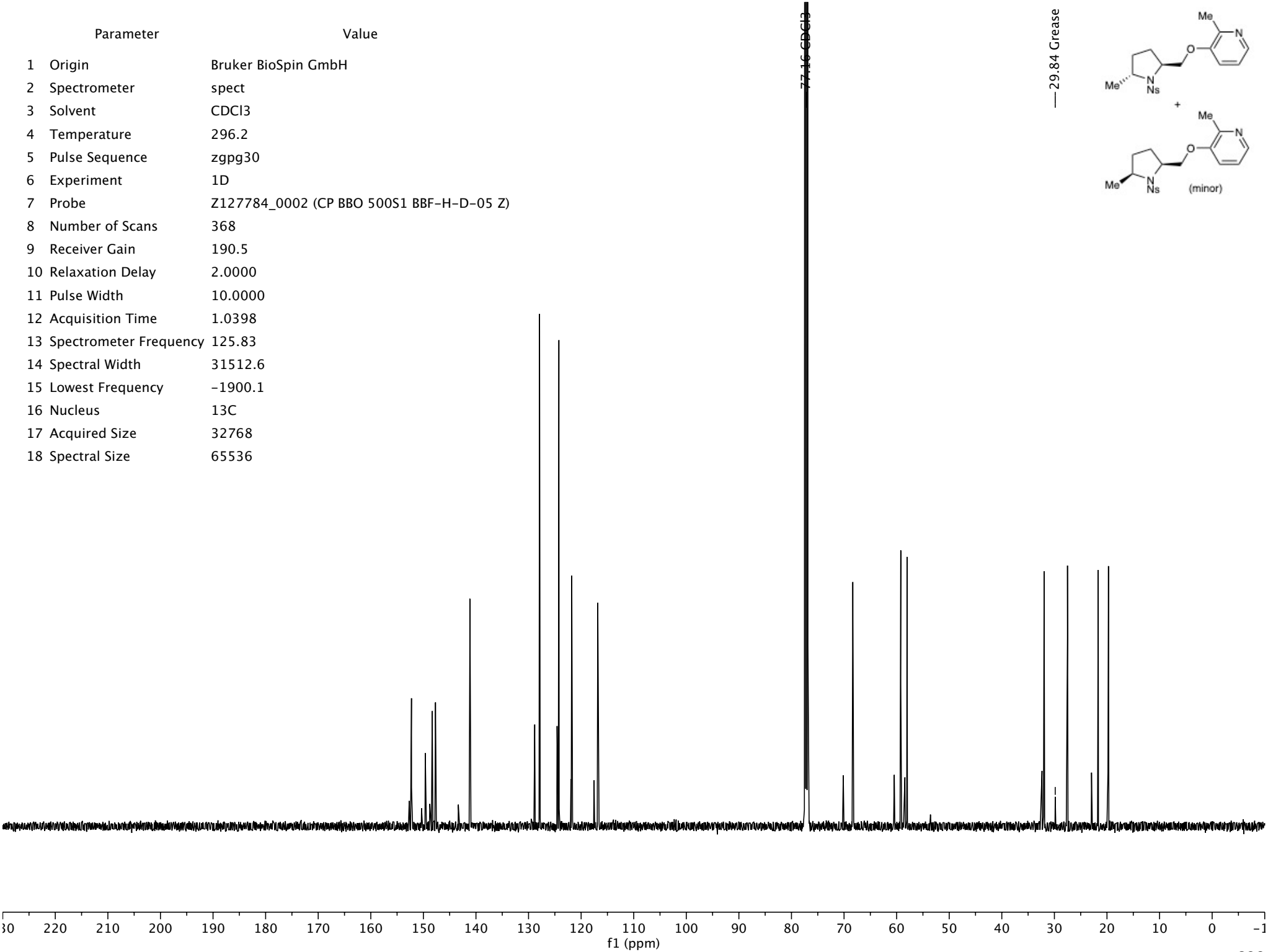
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	2048
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1887.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



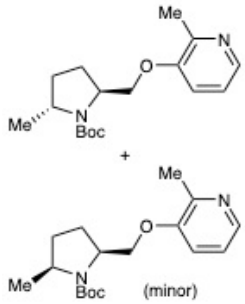
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



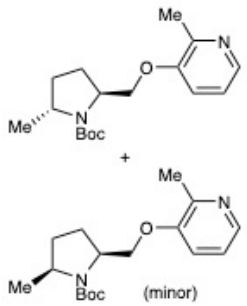
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1900.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	94.3
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.8
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



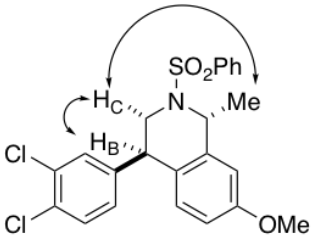
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

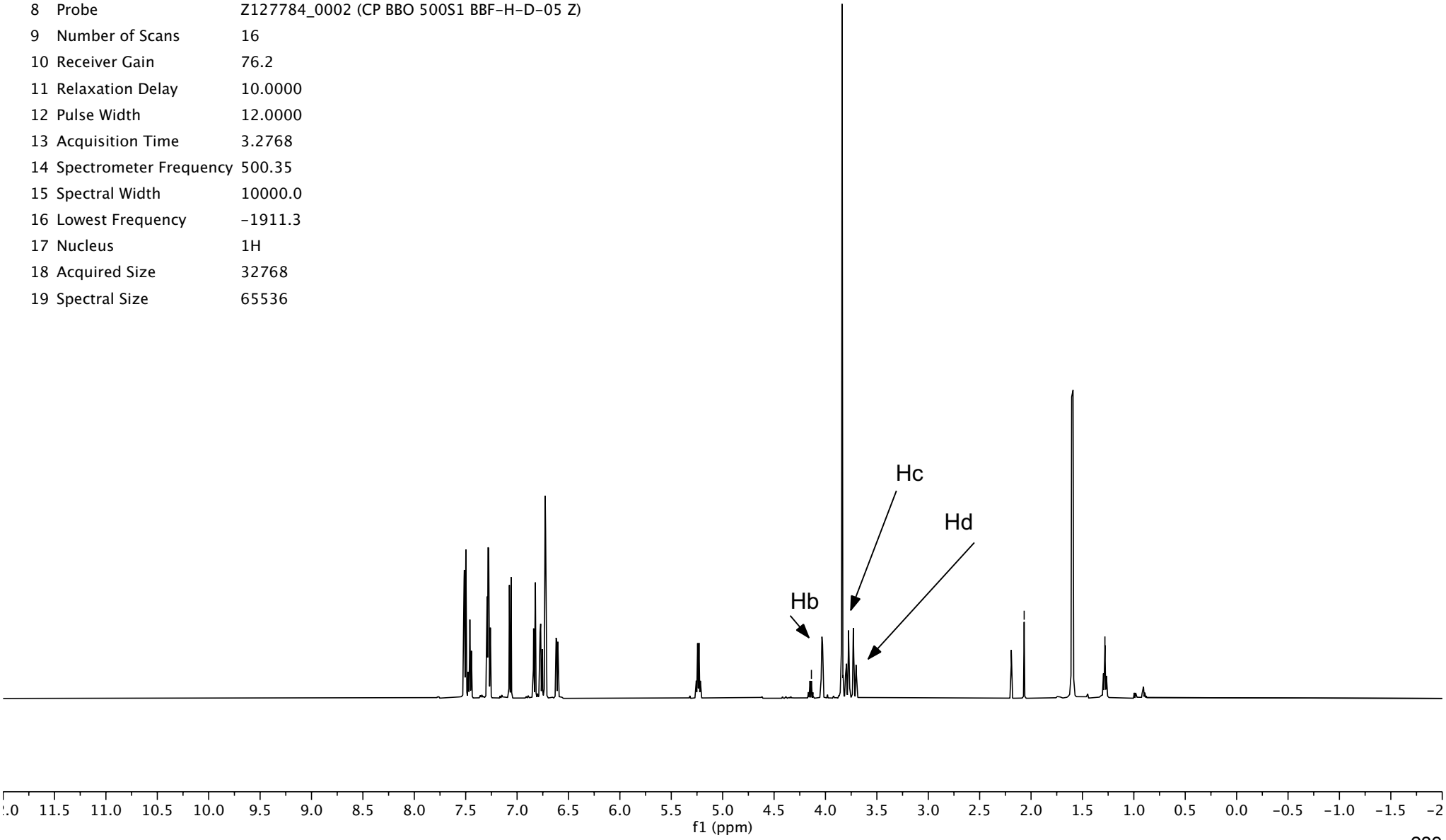


77.16 CDCl3

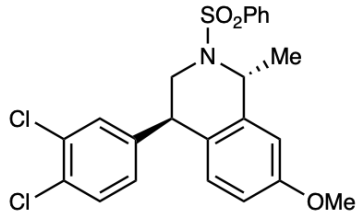
f1 (ppm)

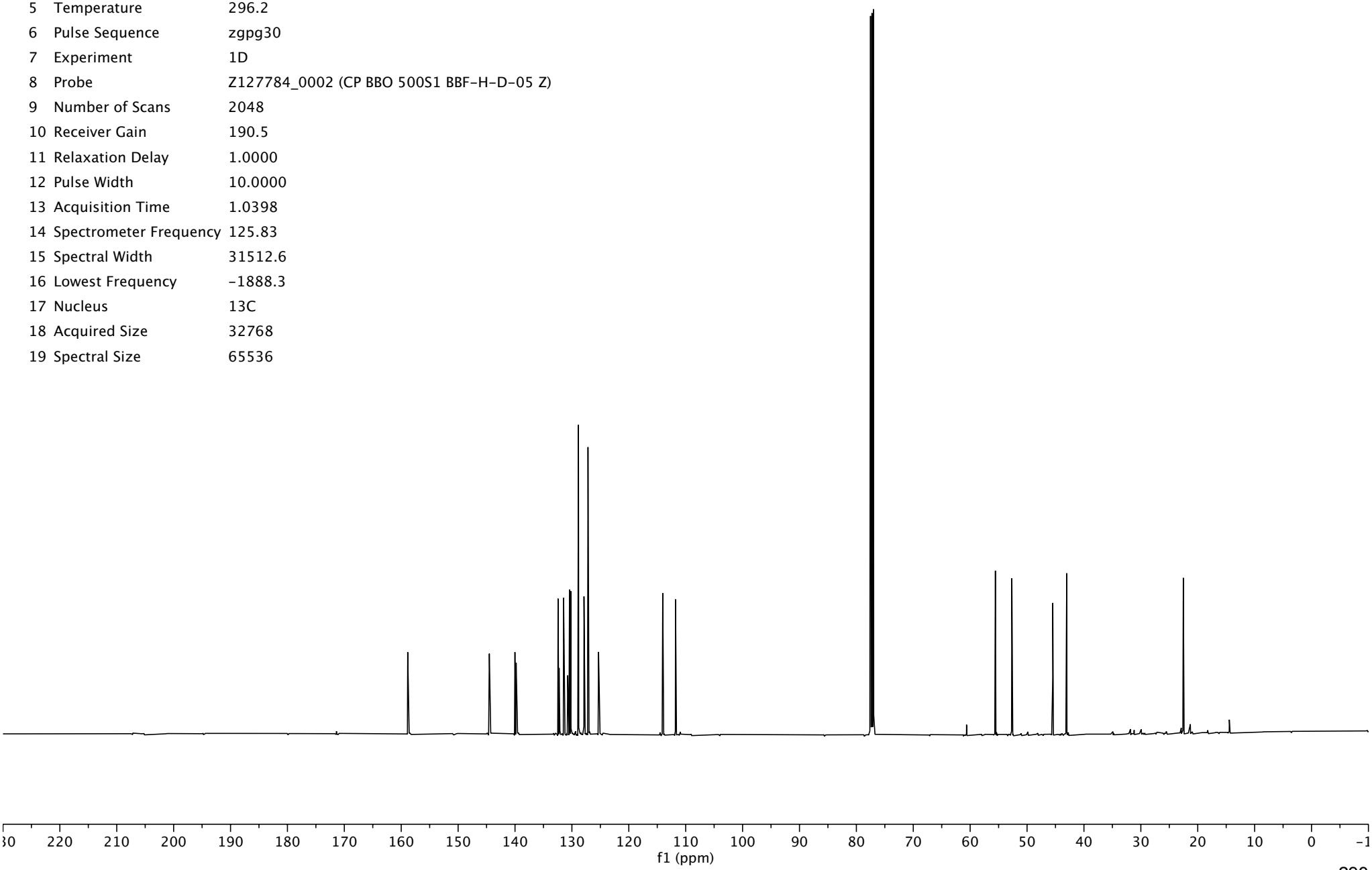
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	76.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1911.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

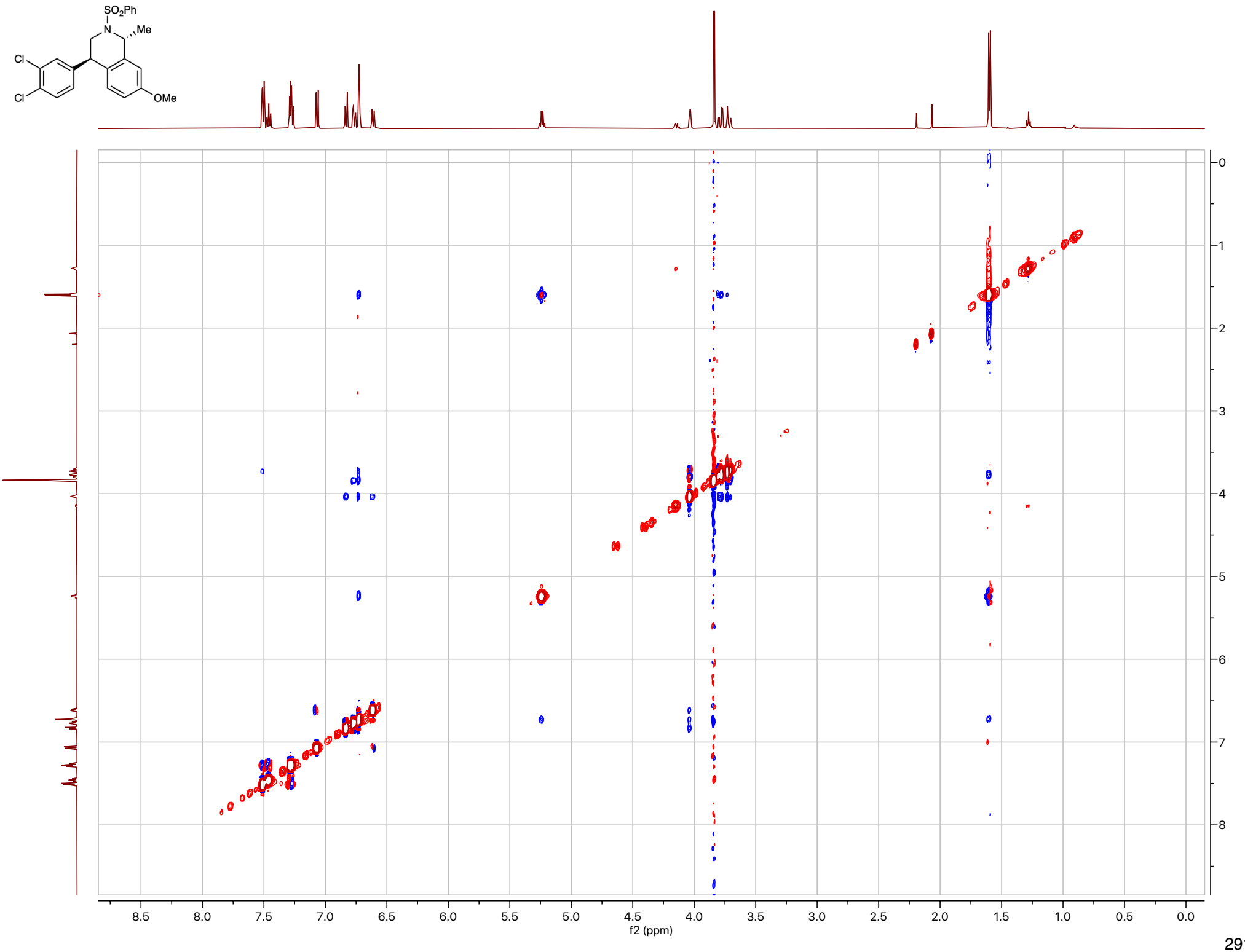


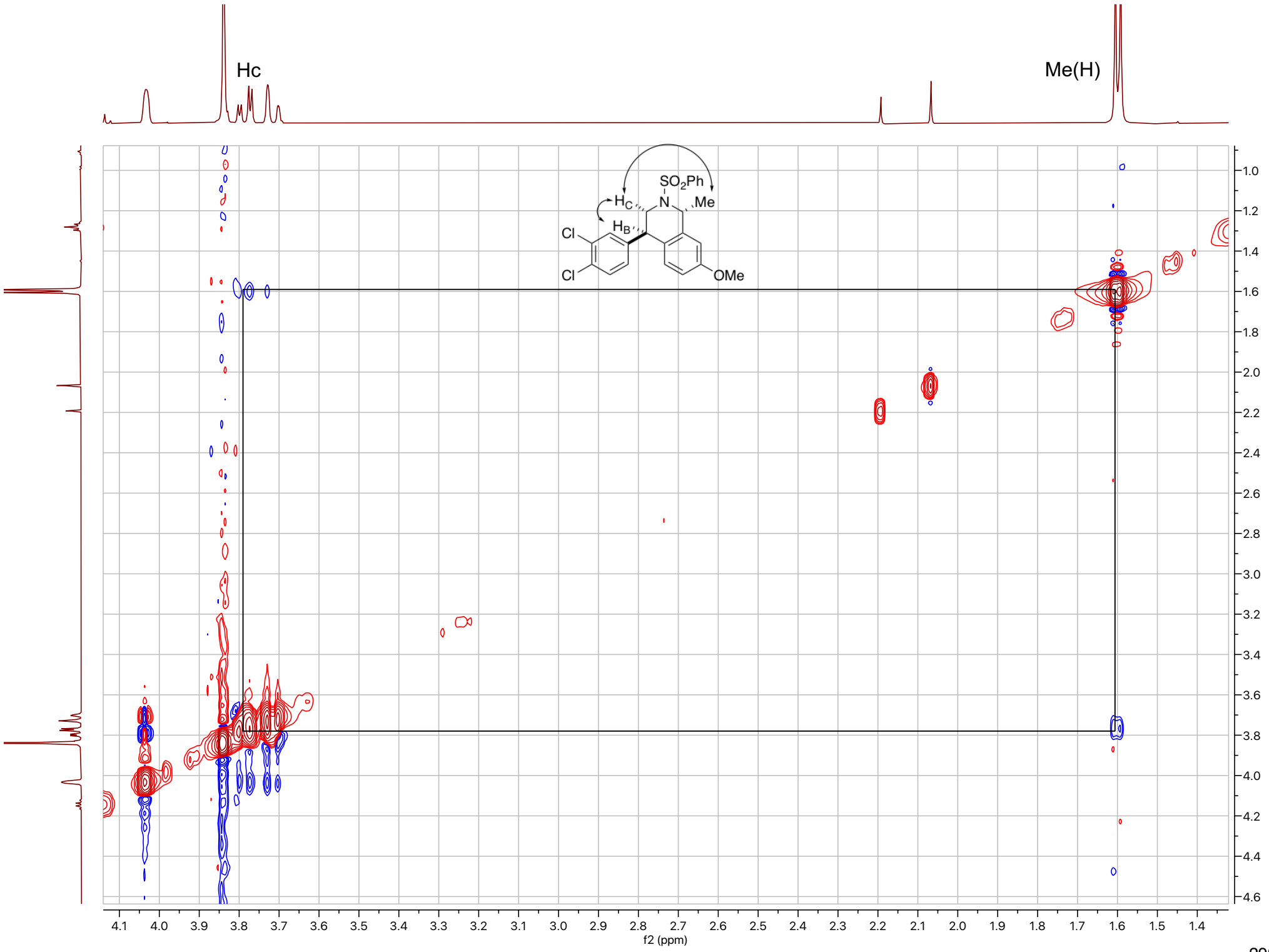


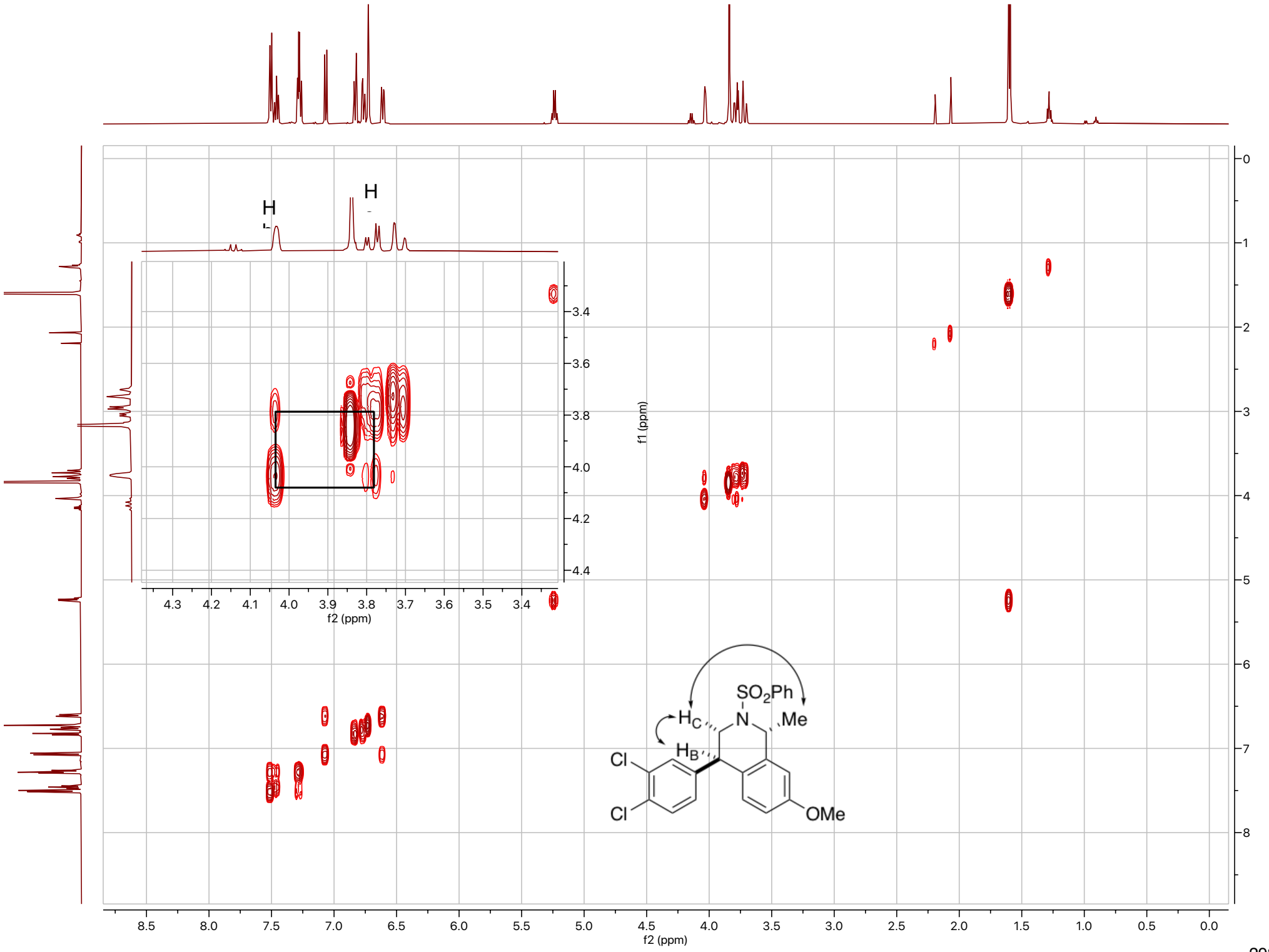
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1888.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



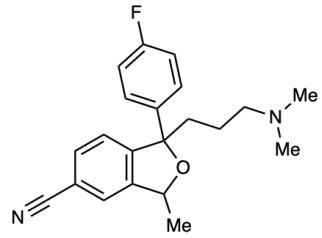



SO2Ph
N
Me
Cl
Cl
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8

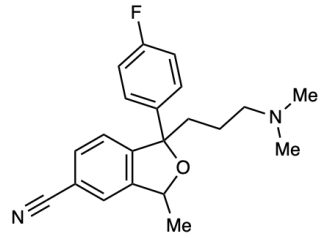

Hc
Me(H)
SO2Ph
N
Me
HC
HB
Cl
Cl
OMe
f2 (ppm)

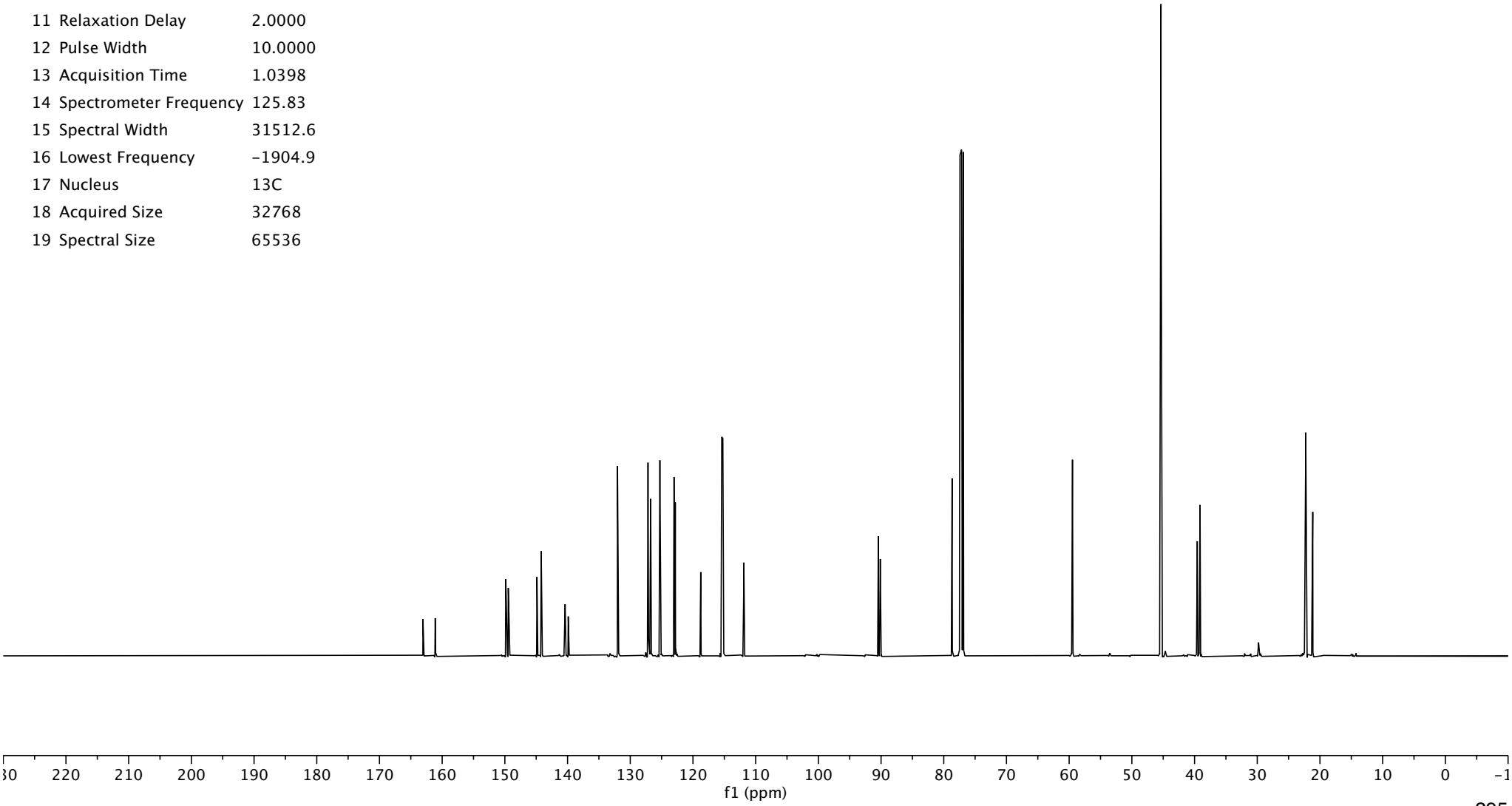

H
H
f2 (ppm)
f1 (ppm)
f2 (ppm)
SO2Ph
N
Me
HC
HB
Cl
Cl
OMe

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1954.1
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

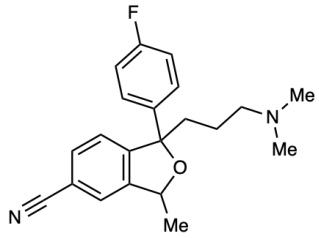


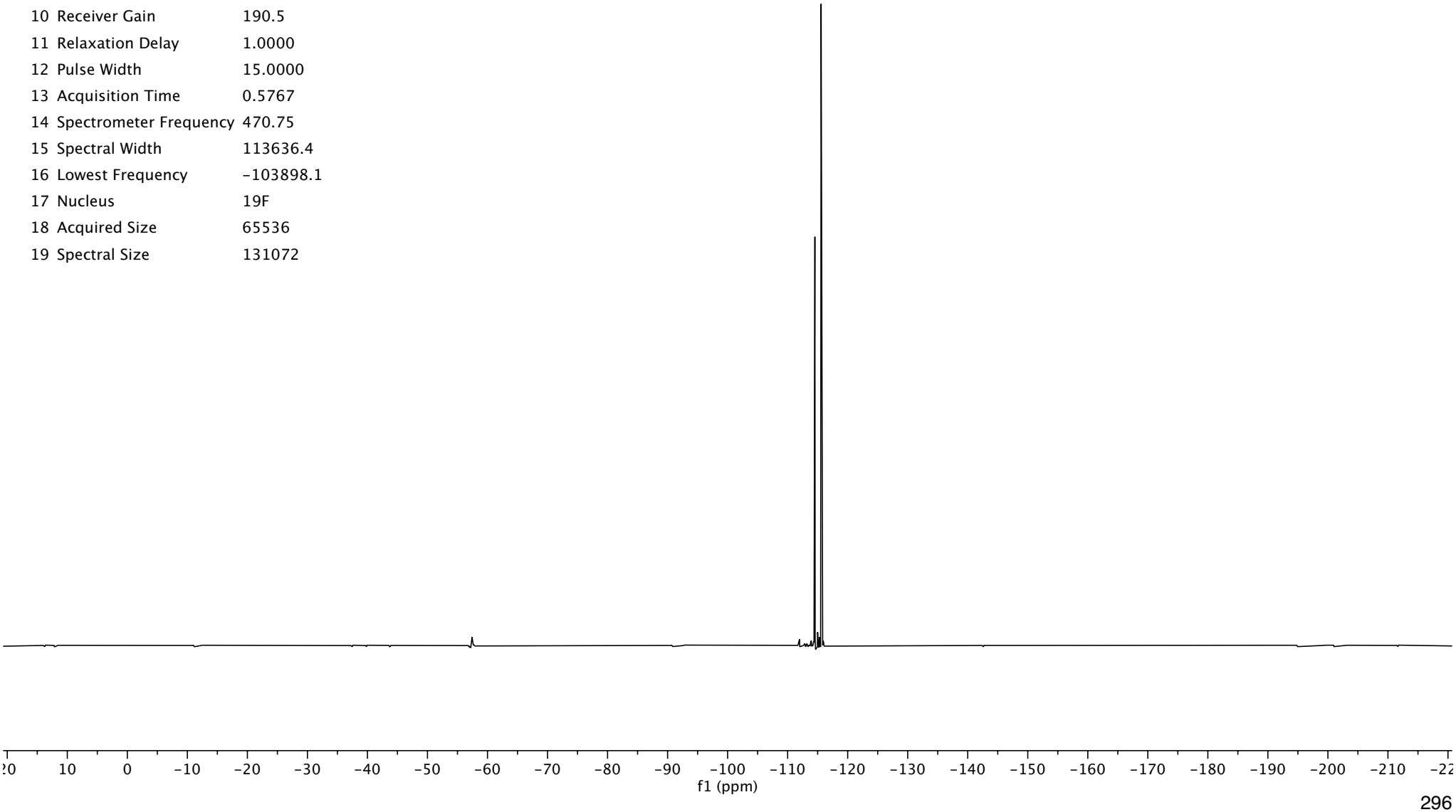
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1904.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



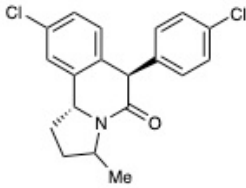


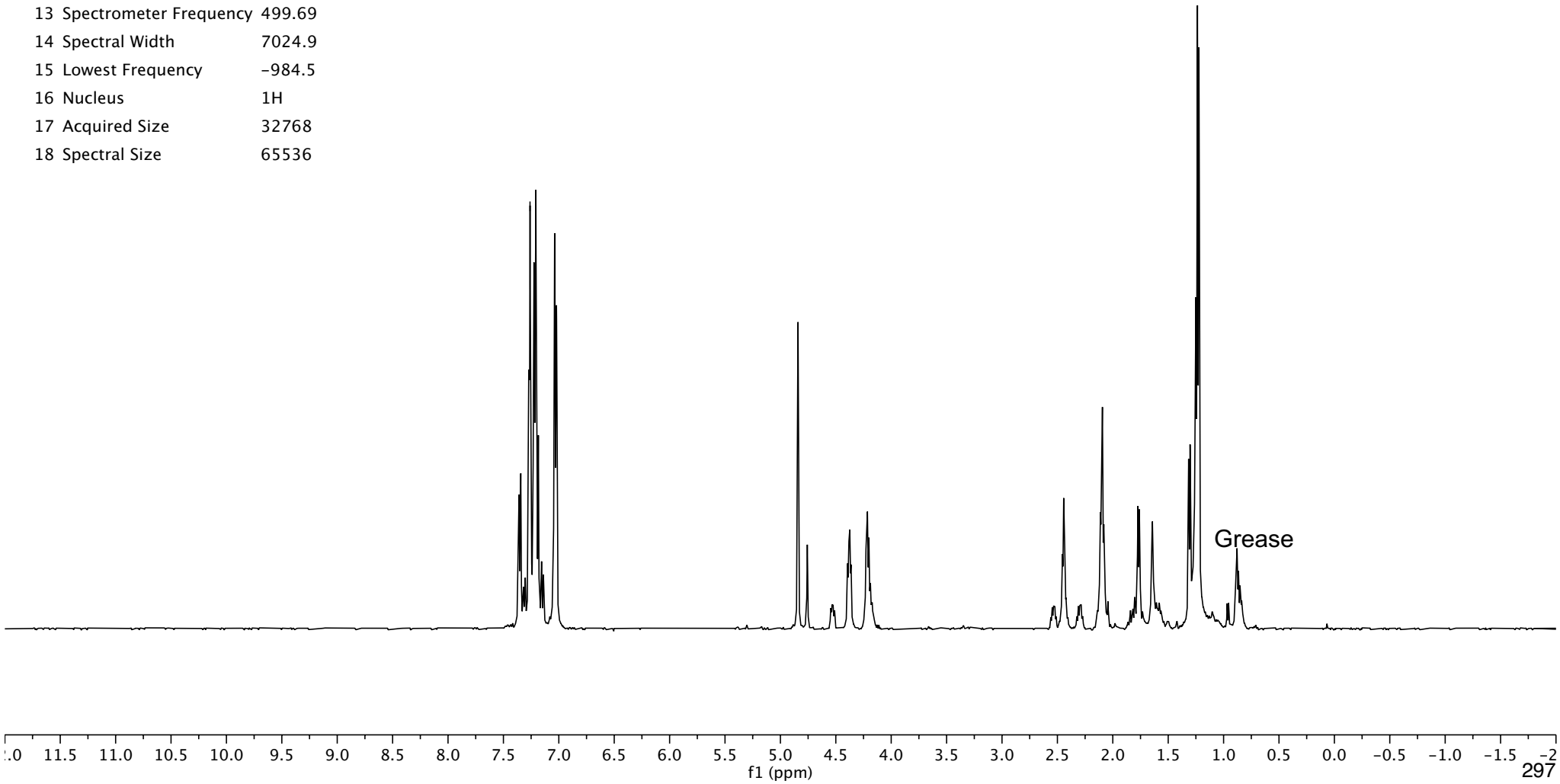
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



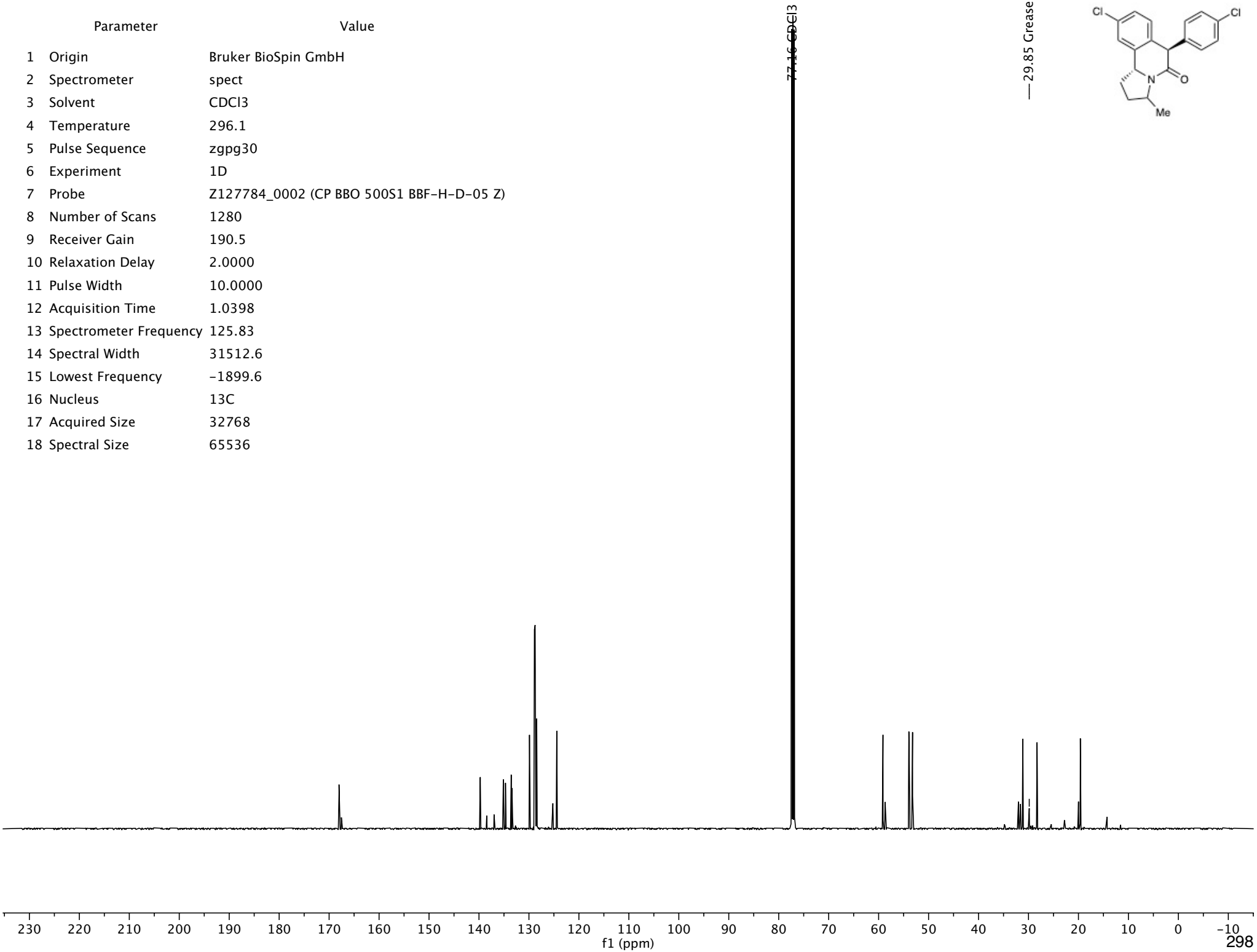


	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	0
9	Receiver Gain	41
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.69
14	Spectral Width	7024.9
15	Lowest Frequency	-984.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

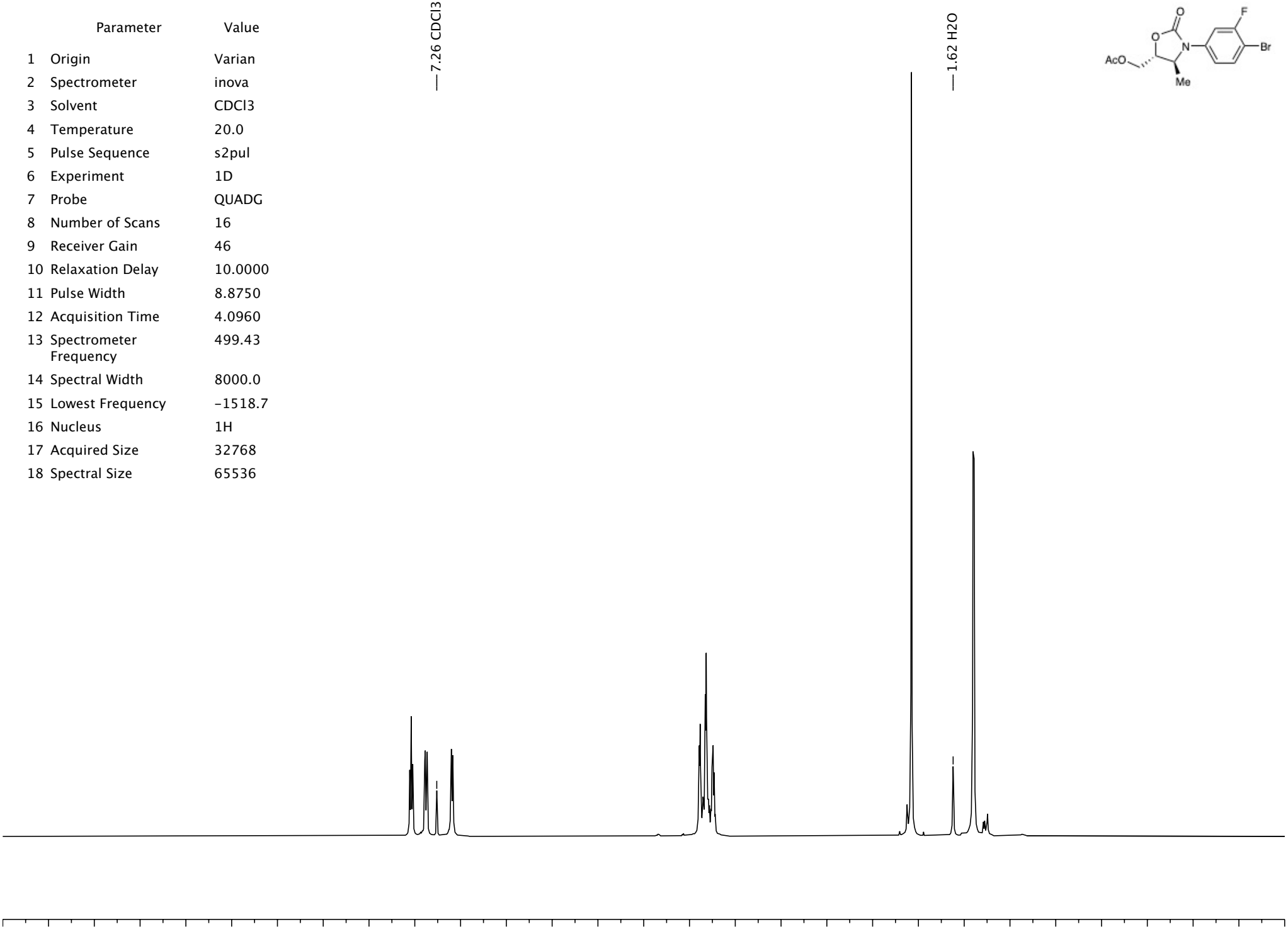




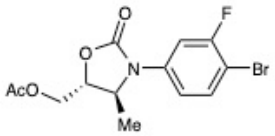
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1280
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



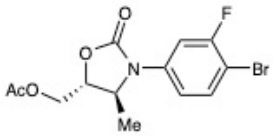
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUADG
8	Number of Scans	16
9	Receiver Gain	46
10	Relaxation Delay	10.0000
11	Pulse Width	8.8750
12	Acquisition Time	4.0960
13	Spectrometer Frequency	499.43
14	Spectral Width	8000.0
15	Lowest Frequency	-1518.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

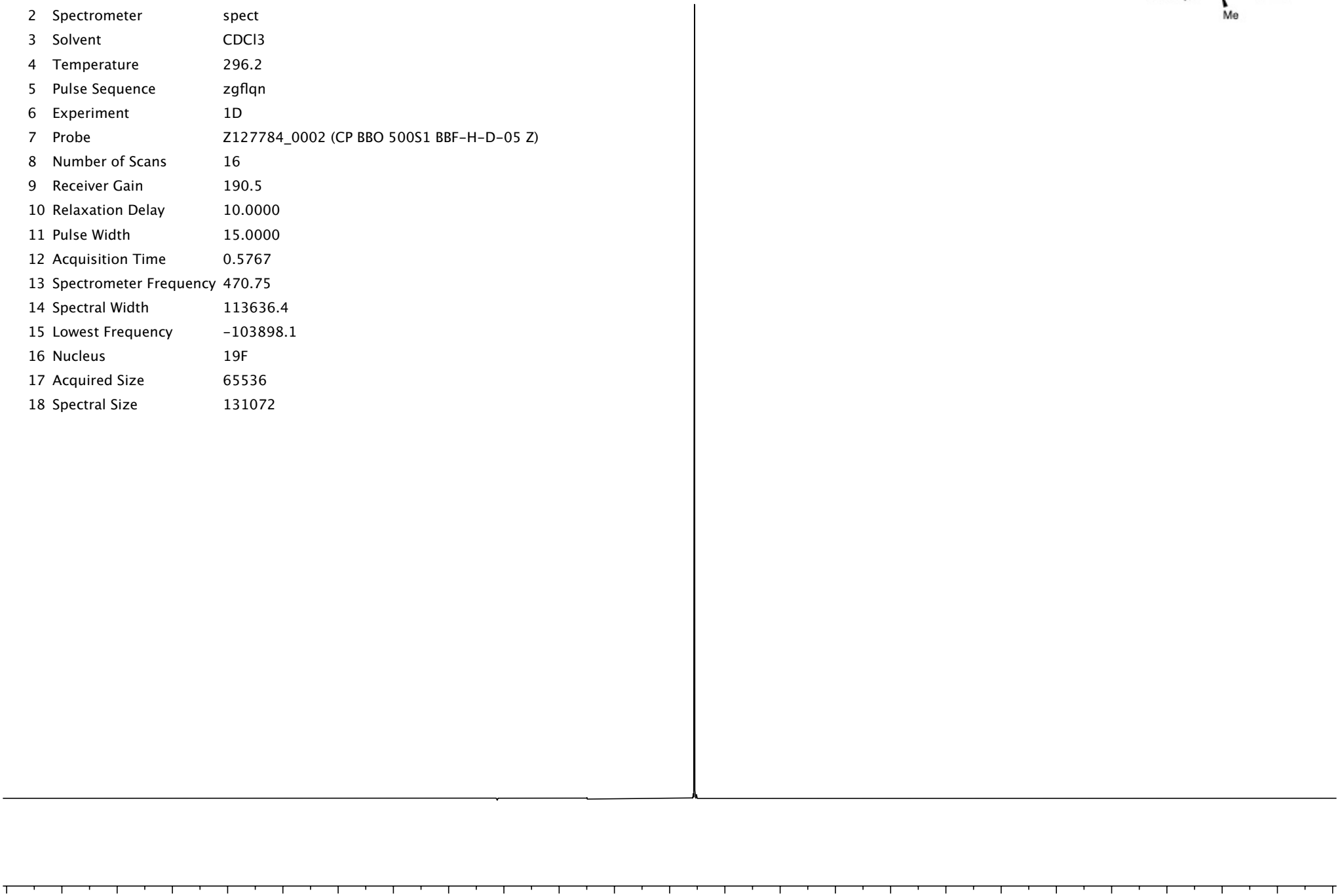


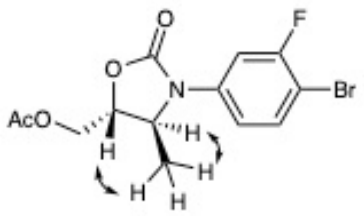
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1902.6
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

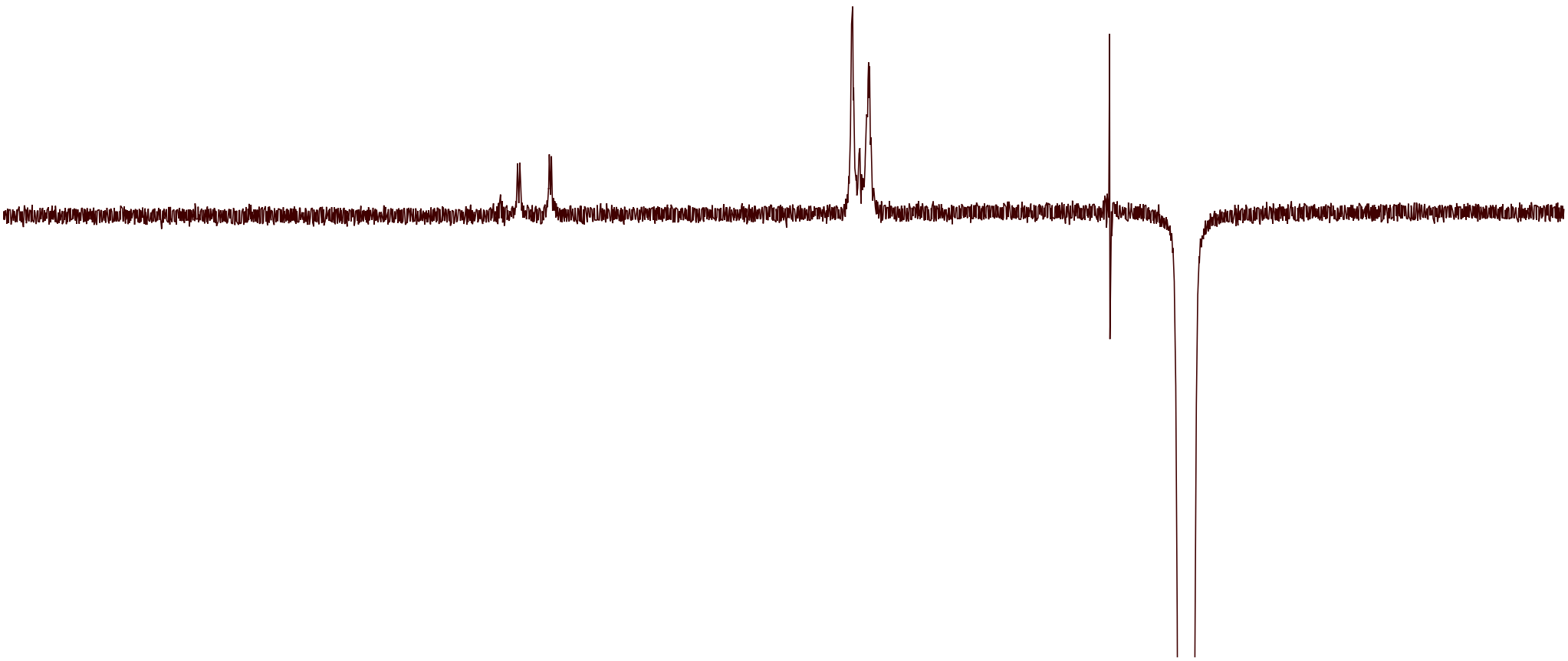


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	15.0000
12	Acquisition Time	0.5767
13	Spectrometer Frequency	470.75
14	Spectral Width	113636.4
15	Lowest Frequency	-103898.1
16	Nucleus	19F
17	Acquired Size	65536
18	Spectral Size	131072





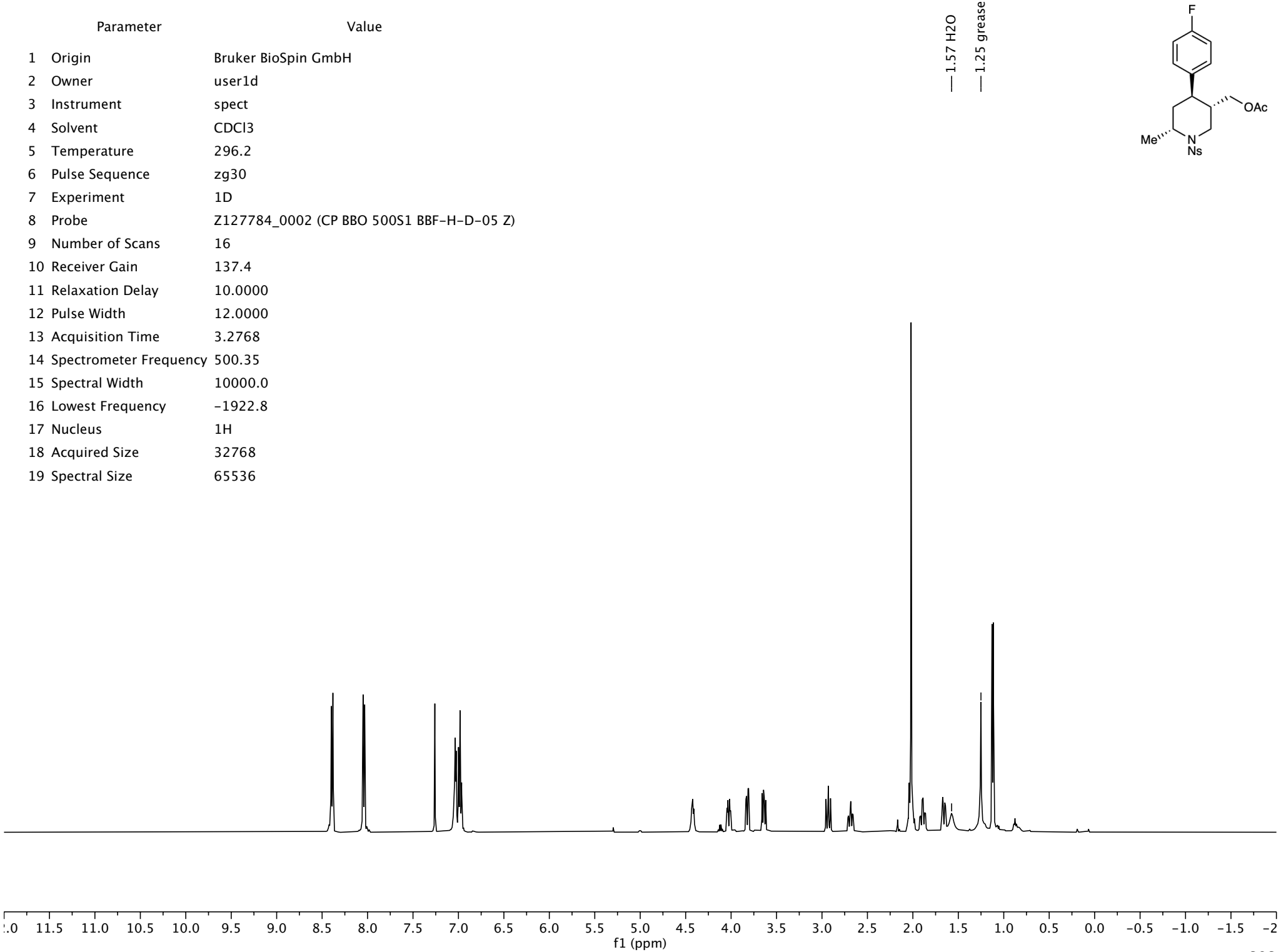




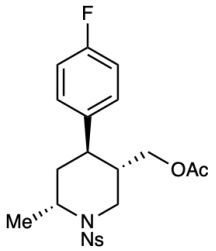
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2

f1 (ppm)

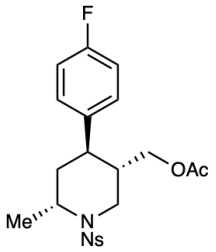
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	137.4
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

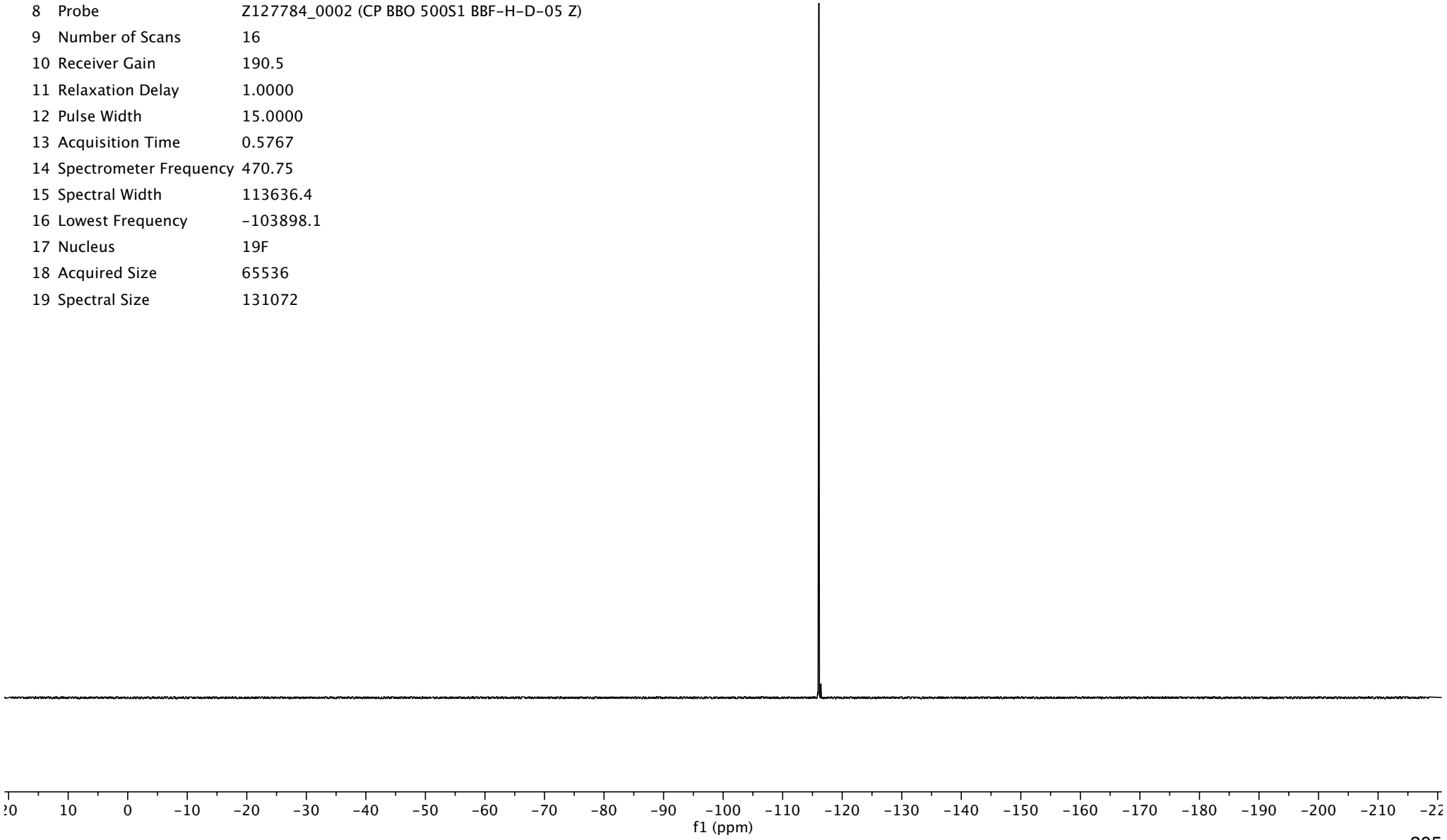


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

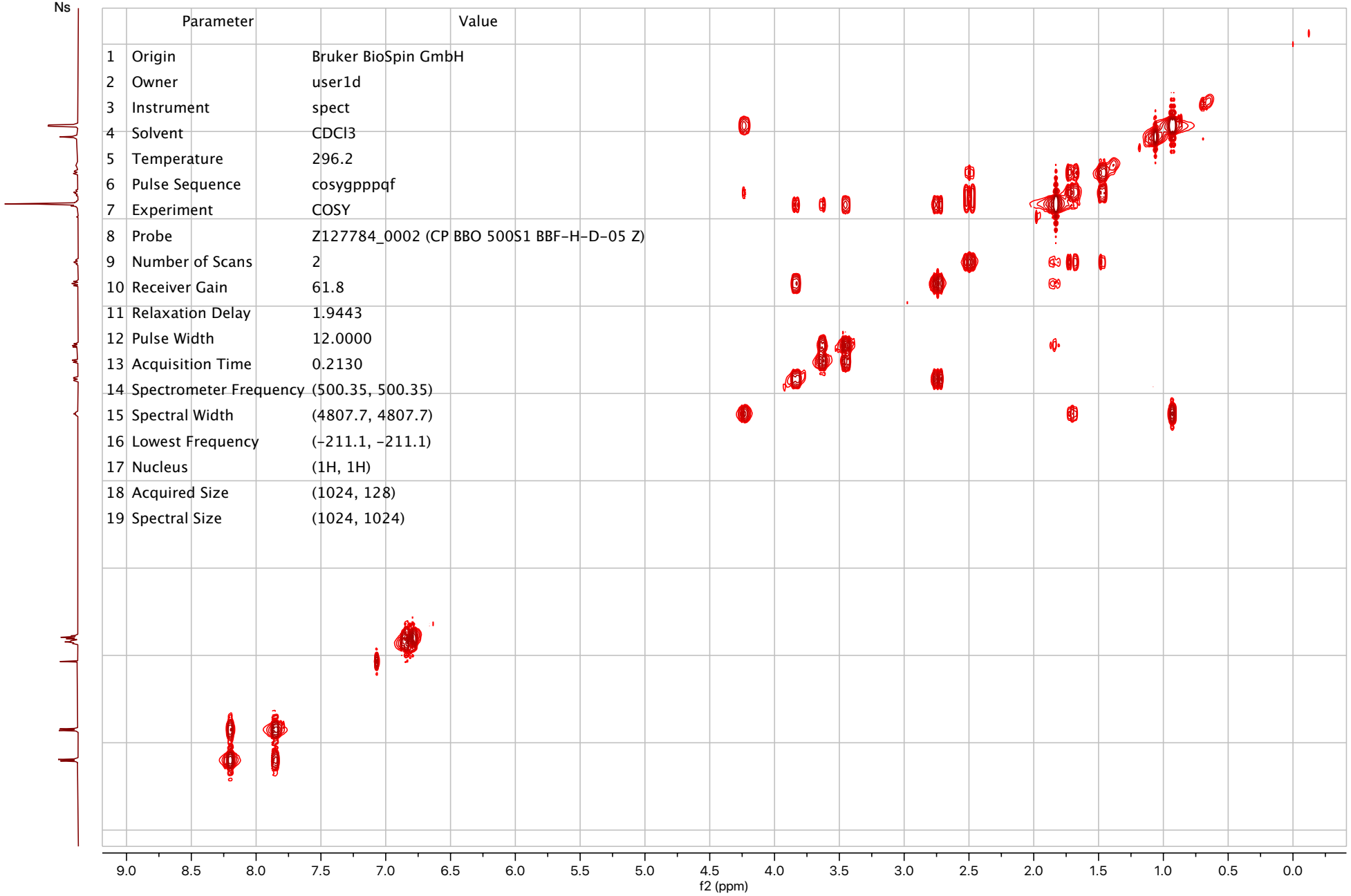


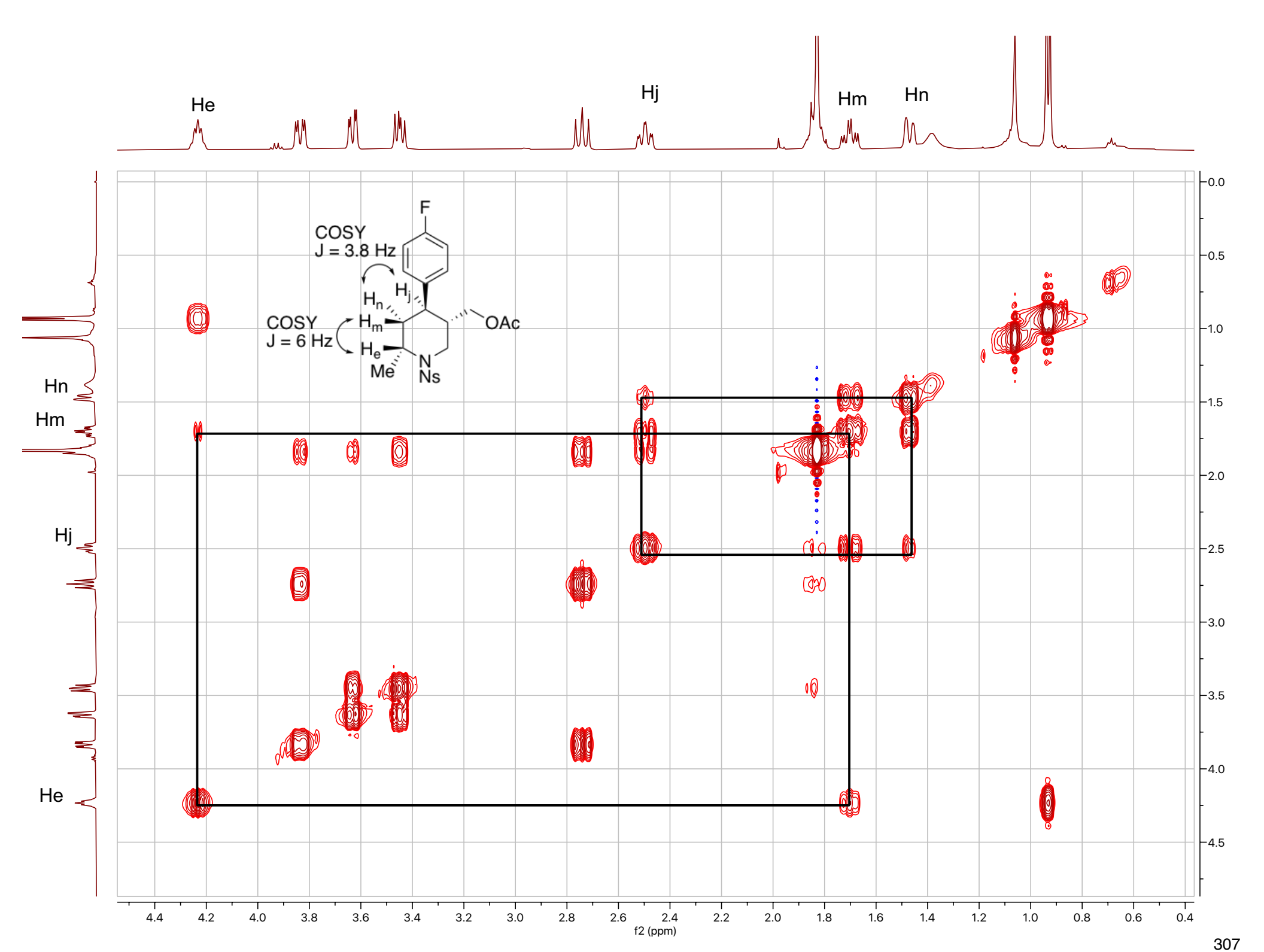
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



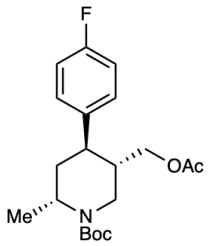


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	cosygpppqf
7	Experiment	COSY
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2
10	Receiver Gain	61.8
11	Relaxation Delay	1.9443
12	Pulse Width	12.0000
13	Acquisition Time	0.2130
14	Spectrometer Frequency	(500.35, 500.35)
15	Spectral Width	(4807.7, 4807.7)
16	Lowest Frequency	(-211.1, -211.1)
17	Nucleus	(1H, 1H)
18	Acquired Size	(1024, 128)
19	Spectral Size	(1024, 1024)

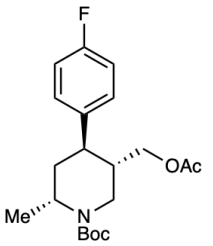



He
Hj
Hm
Hn
COSY
J = 3.8 Hz
COSY
J = 6 Hz
F
OAc
N
Ns
Me
f2 (ppm)

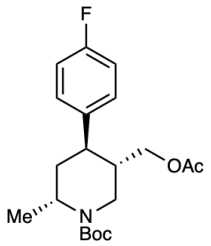
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.5
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

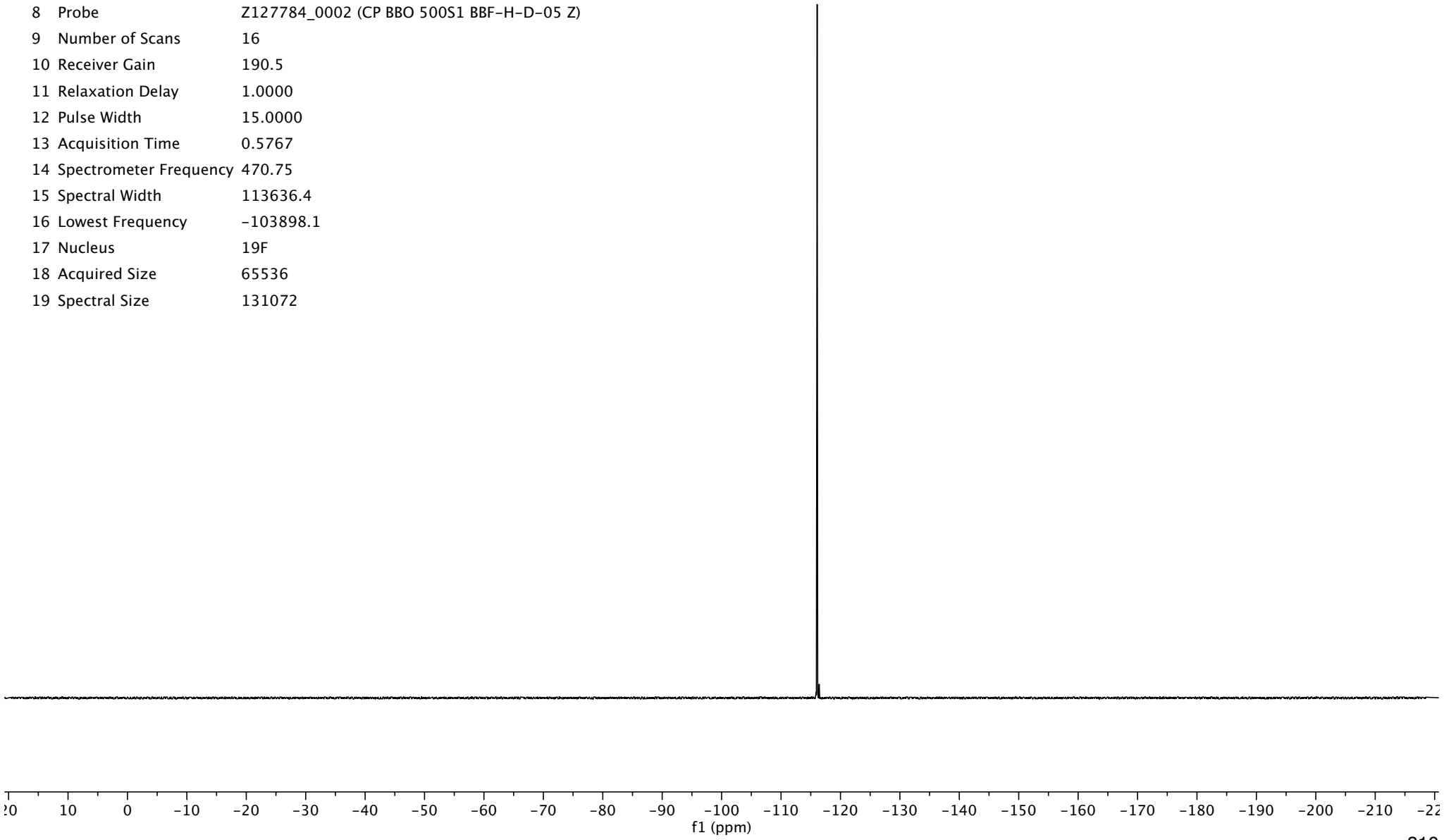


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1900.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



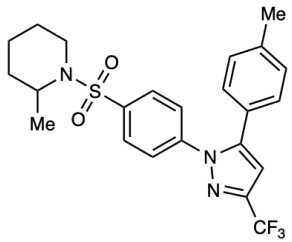
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

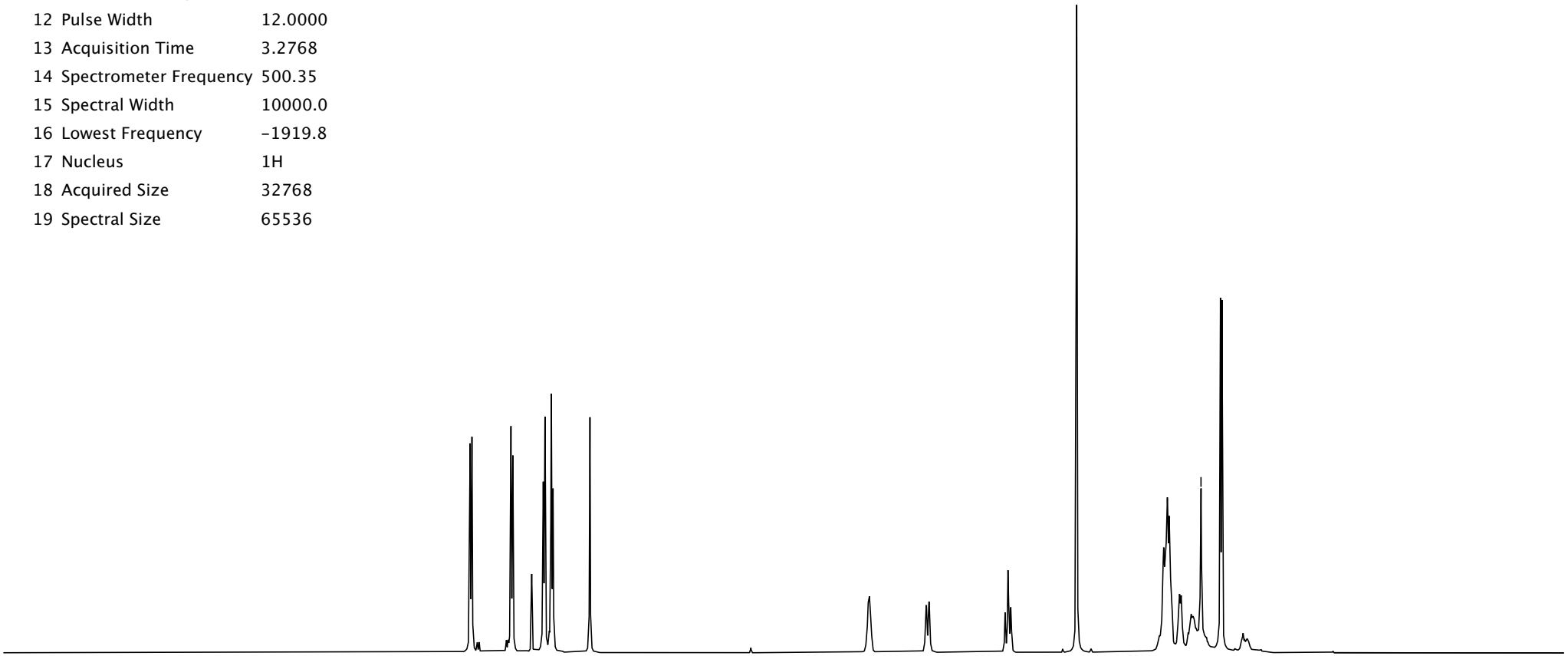


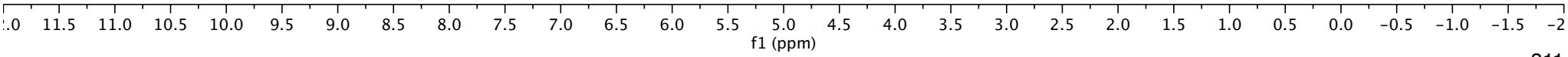


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

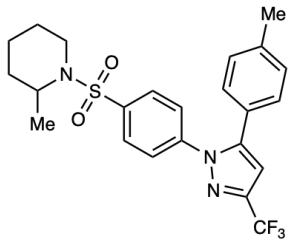
— 1.26 grease

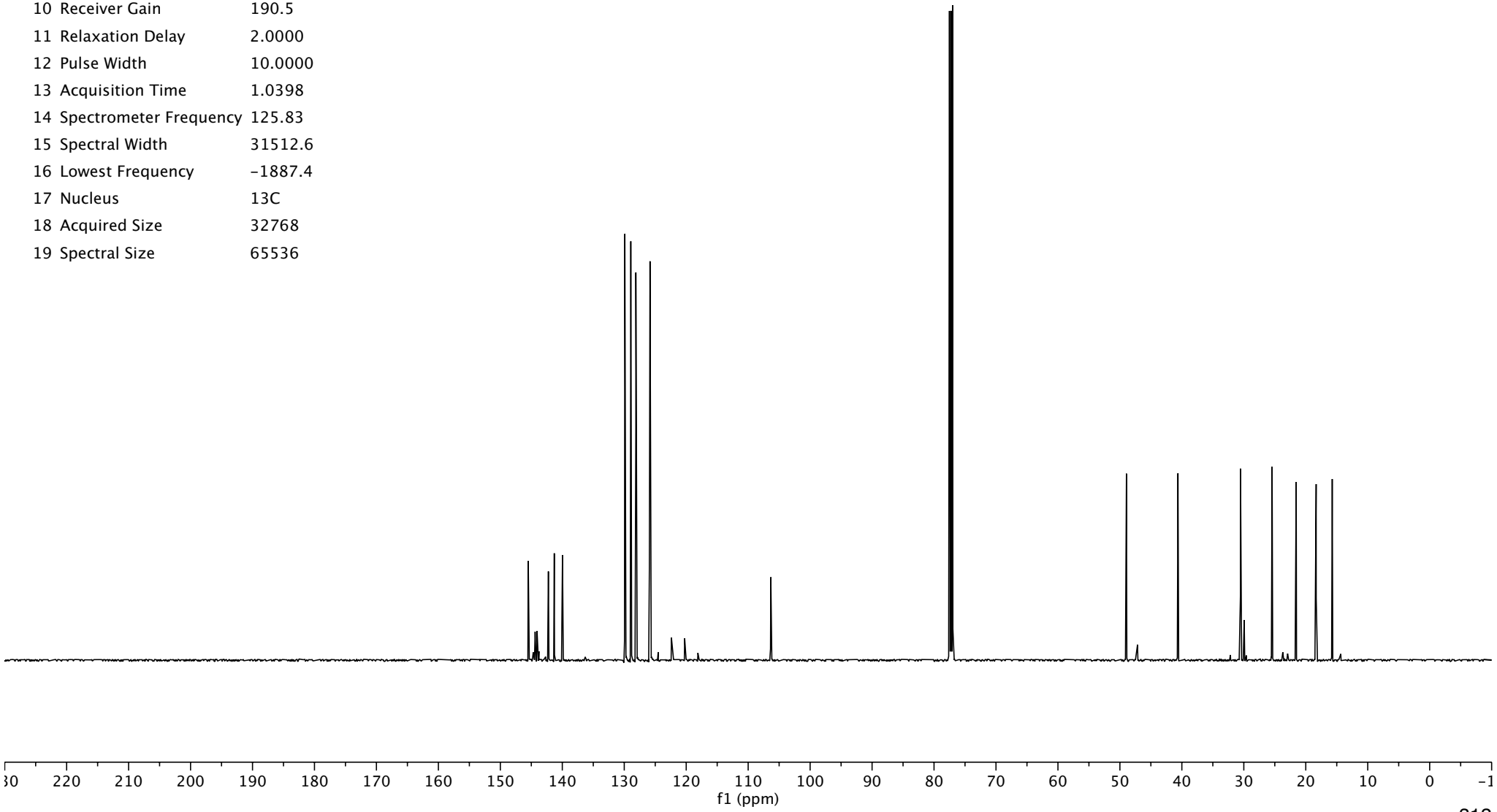




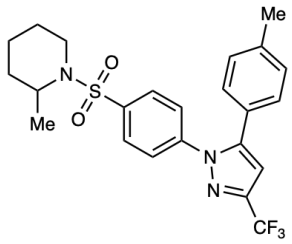


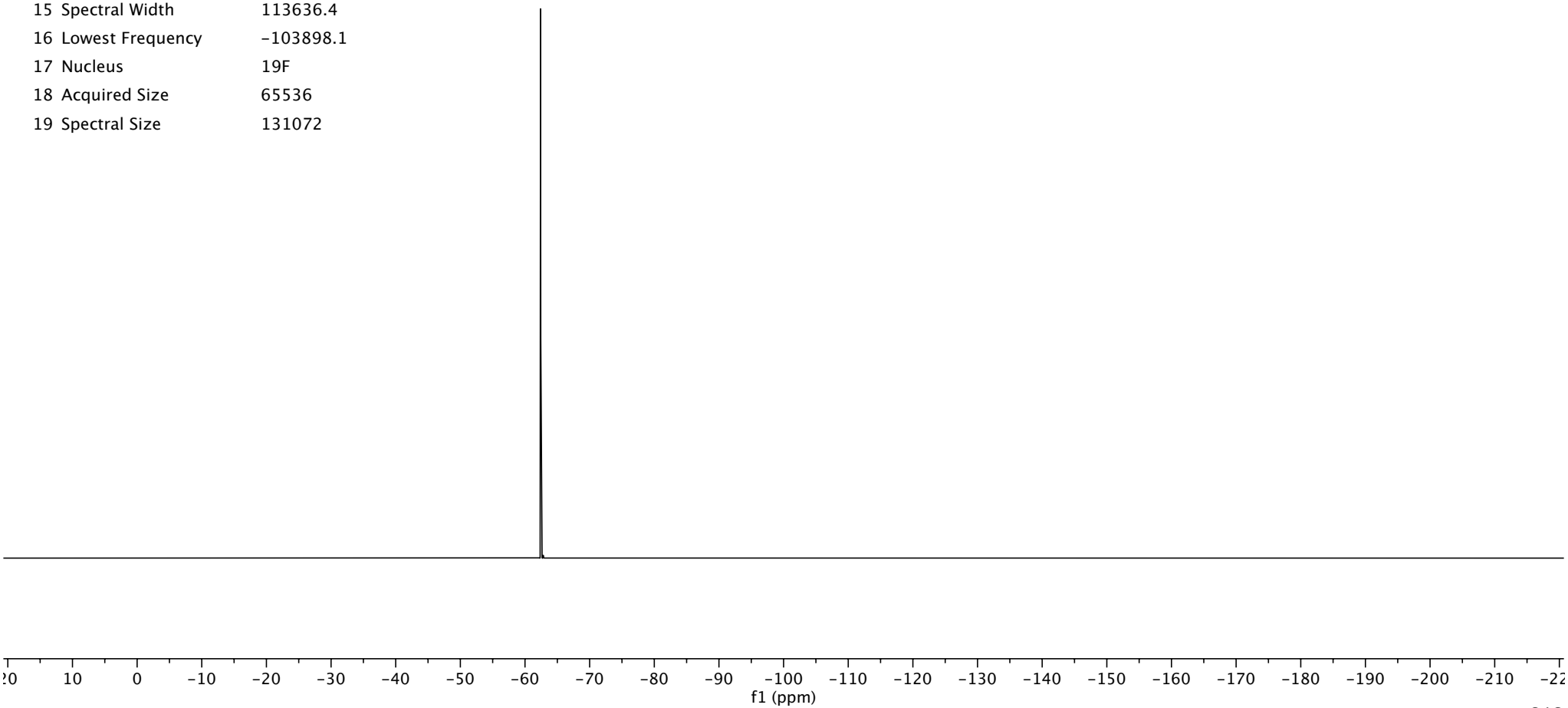
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1887.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



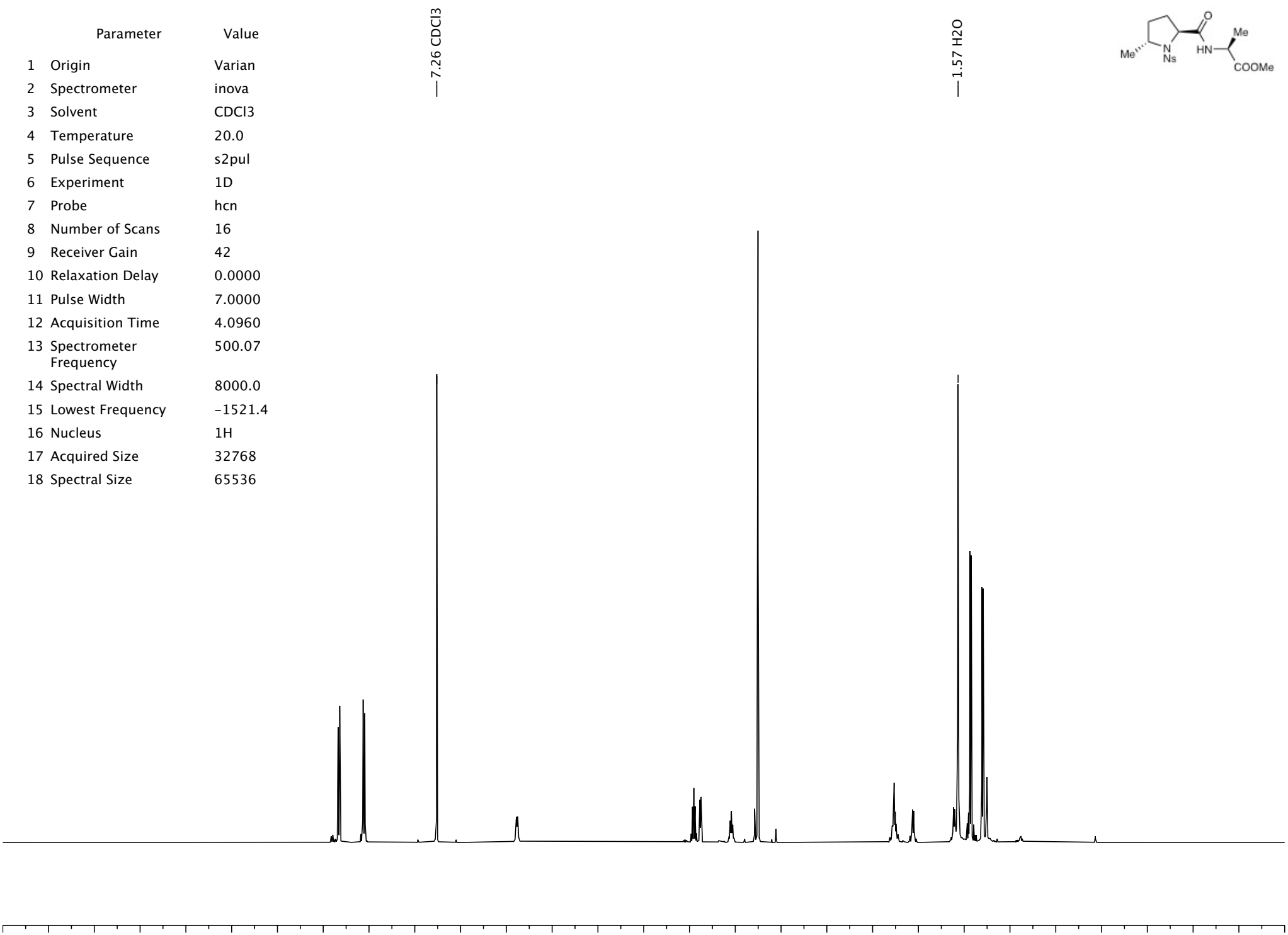


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

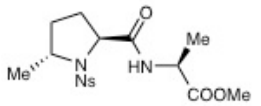


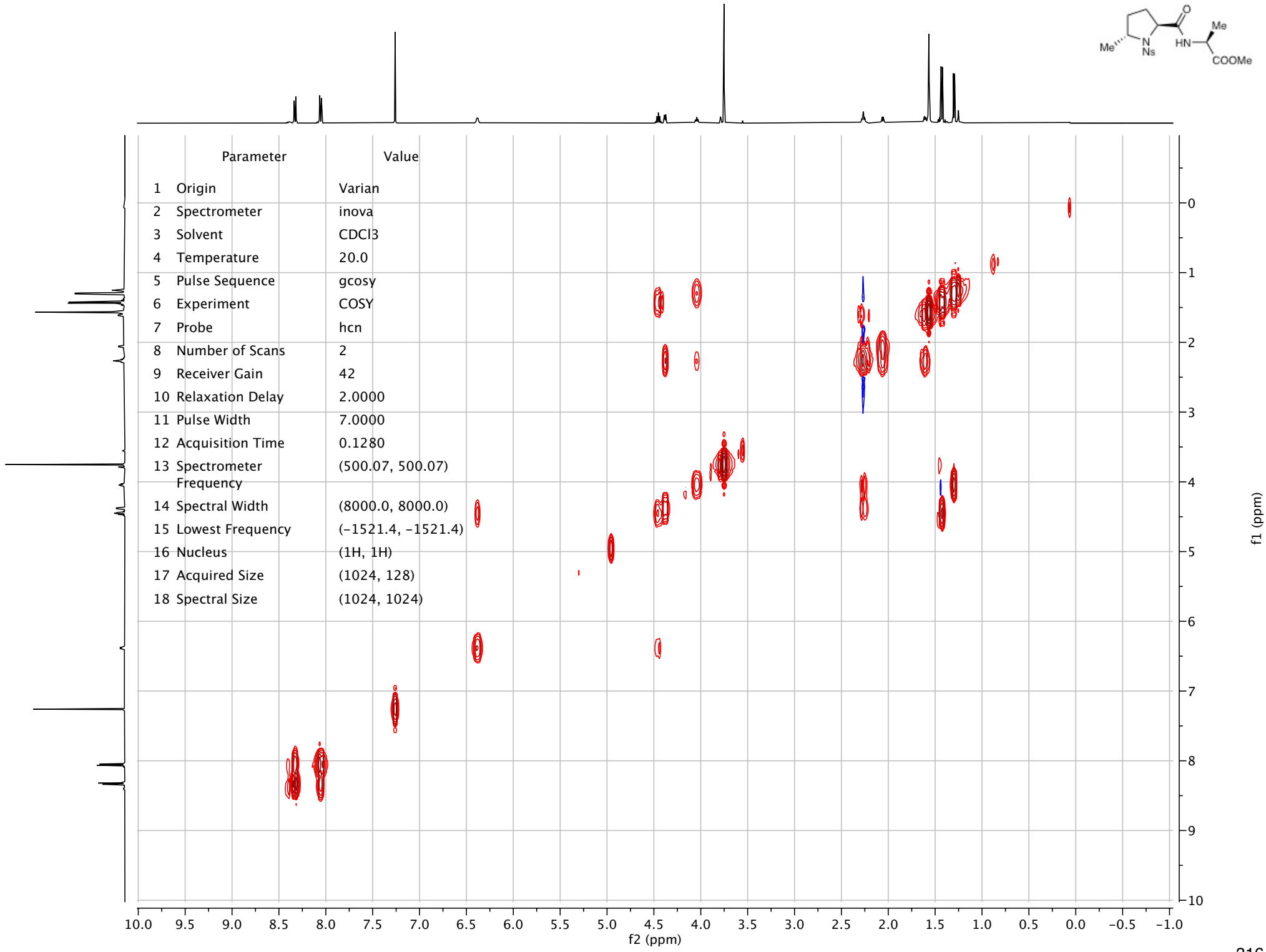


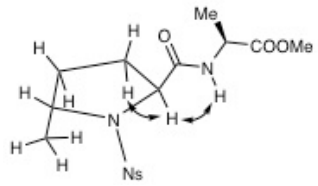
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	0.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.0
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1280
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

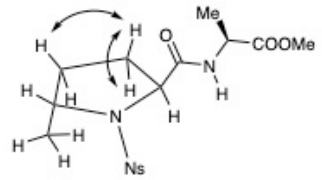


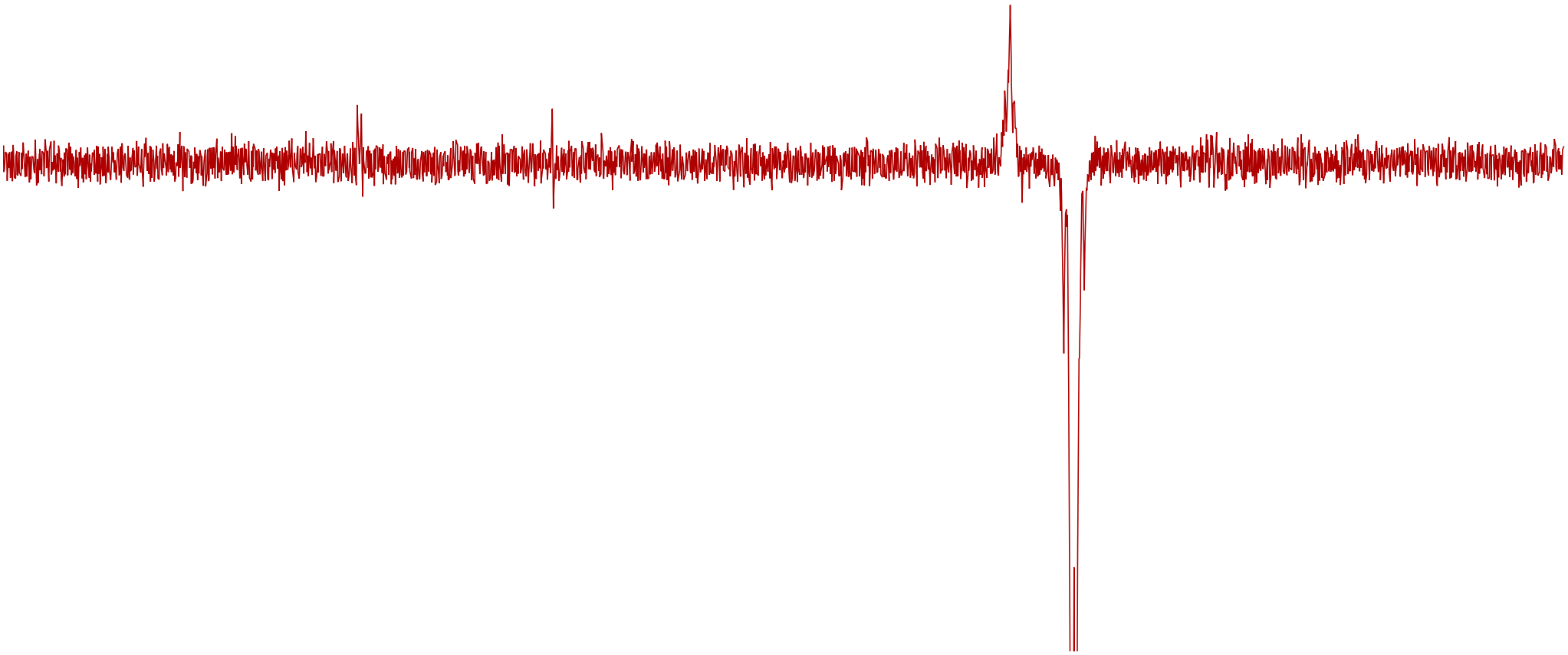

Parameter Value
1 Origin Varian
2 Spectrometer inova
3 Solvent CDCl3
4 Temperature 20.0
5 Pulse Sequence gcosy
6 Experiment COSY
7 Probe hcn
8 Number of Scans 2
9 Receiver Gain 42
10 Relaxation Delay 2.0000
11 Pulse Width 7.0000
12 Acquisition Time 0.1280
13 Spectrometer Frequency (500.07, 500.07)
14 Spectral Width (8000.0, 8000.0)
15 Lowest Frequency (-1521.4, -1521.4)
16 Nucleus (1H, 1H)
17 Acquired Size (1024, 128)
18 Spectral Size (1024, 1024)
Me
N
Ns
HN
O
Me
COOMe
f2 (ppm)
f1 (ppm)



6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2

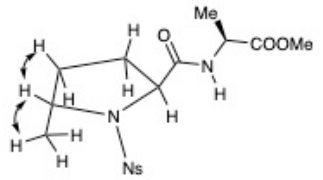
f1 (ppm)





5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6

f1 (ppm)

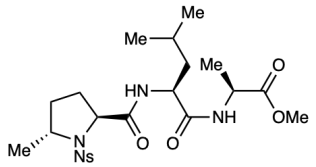


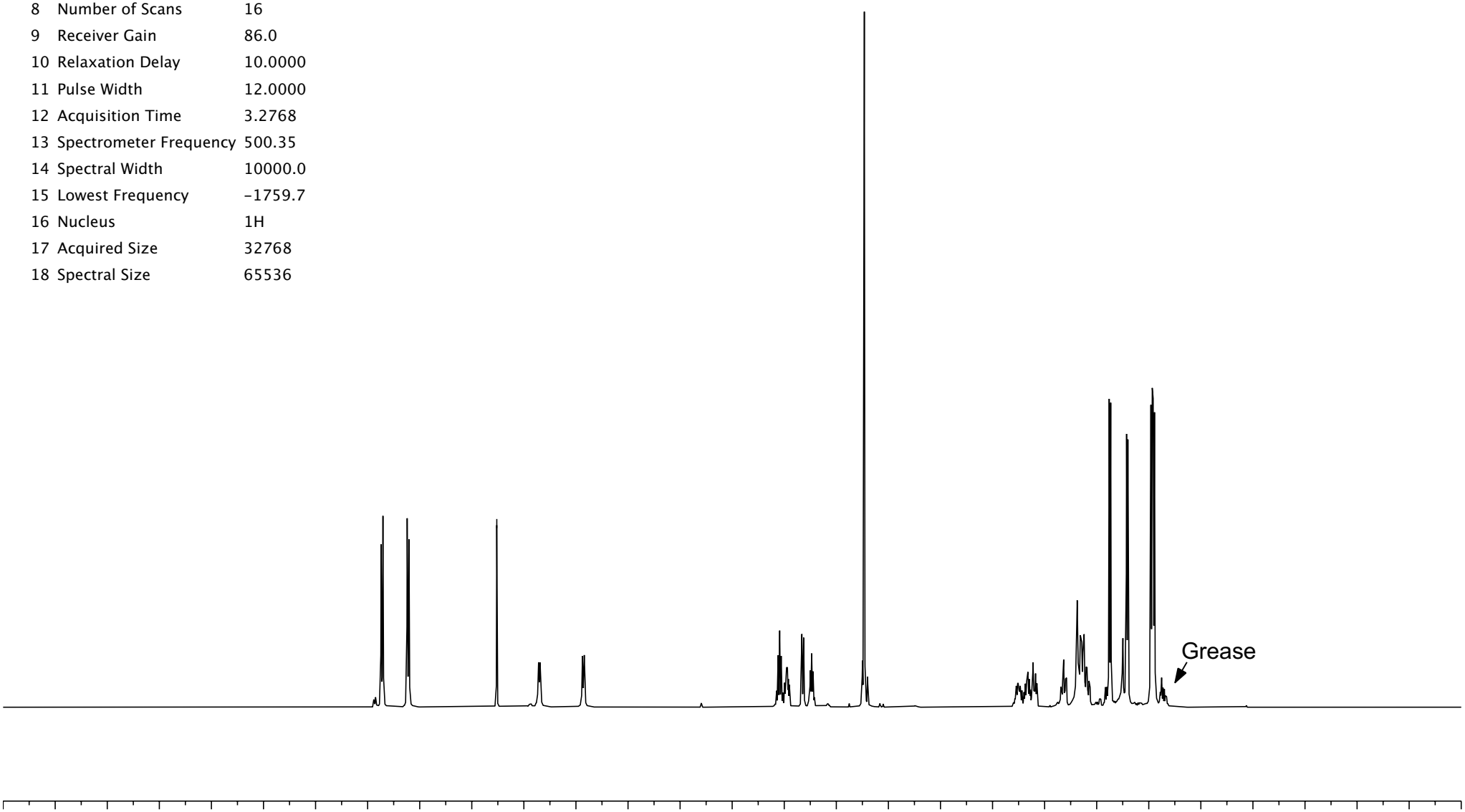
4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.

f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	86.0
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1759.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

7.26 CDCl3

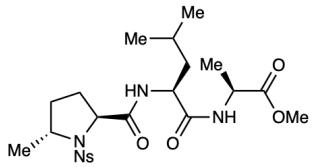




11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2

f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.4
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

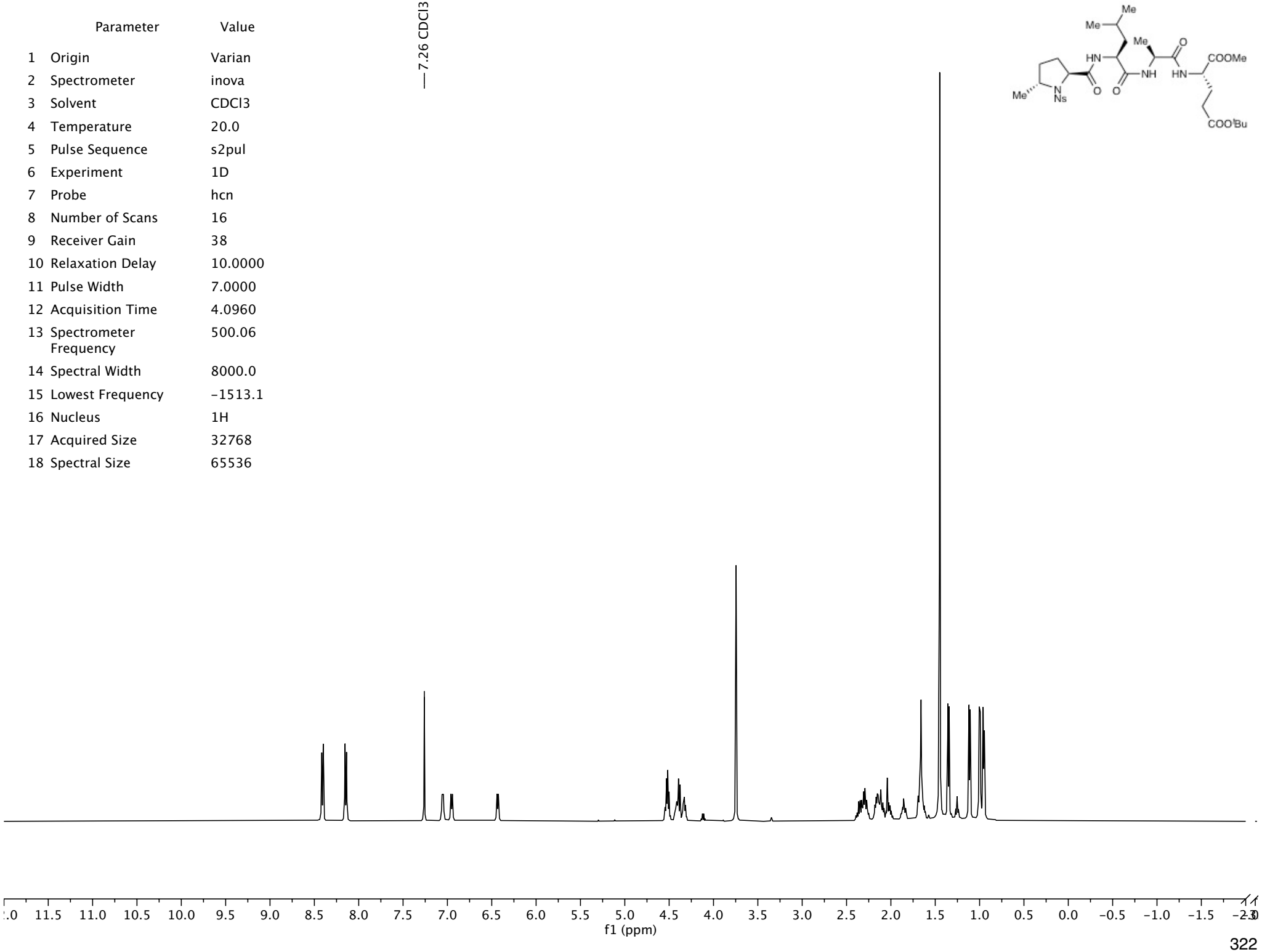


77.16 CDCl3

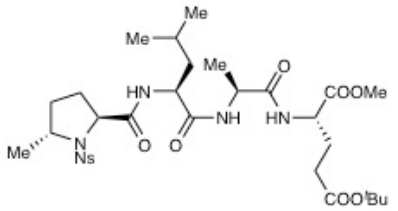
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1280
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

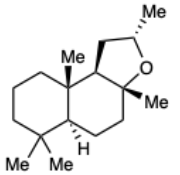


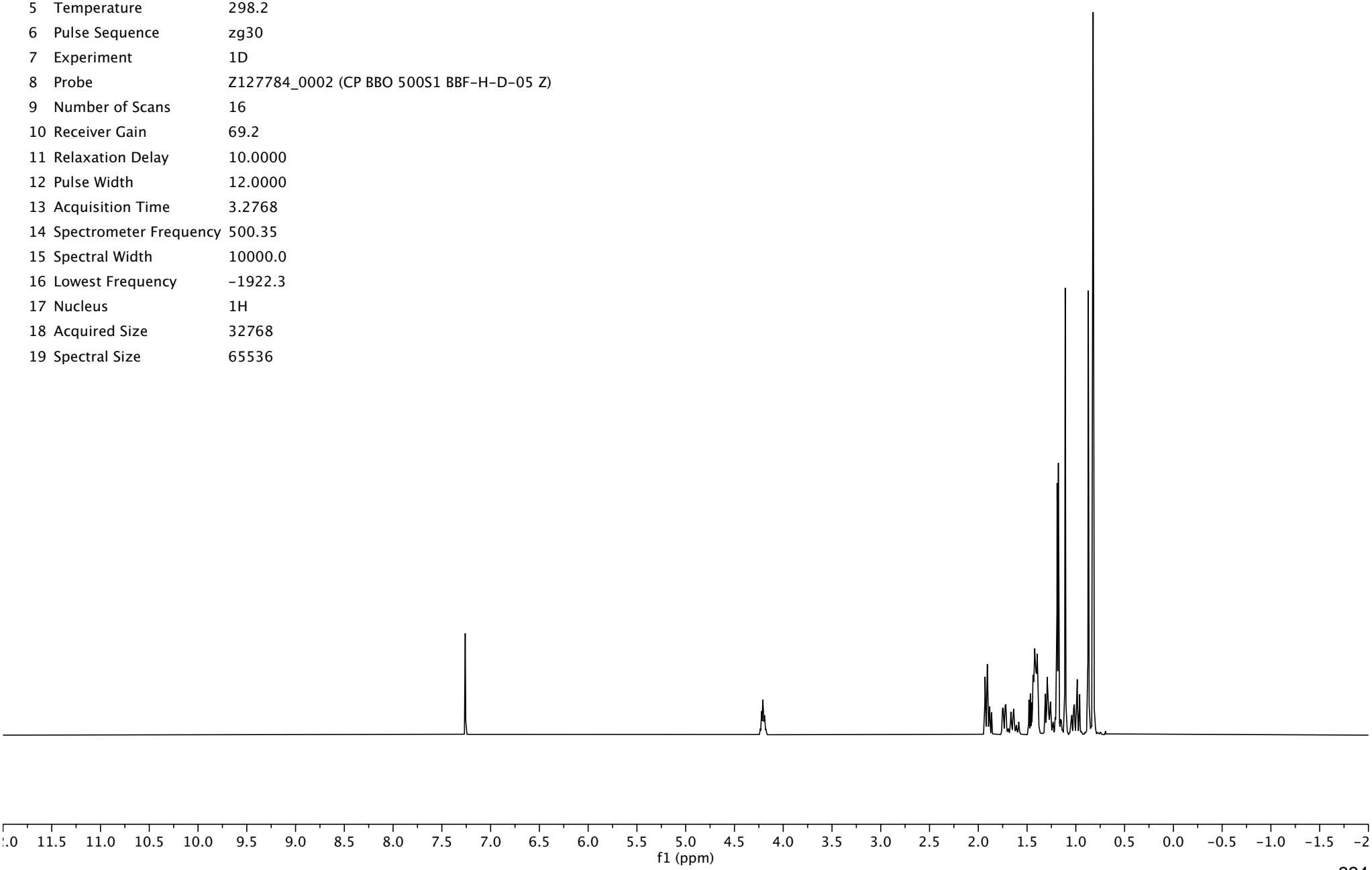
77.16 CDCl3

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

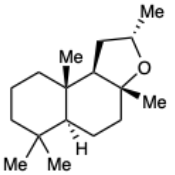
f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

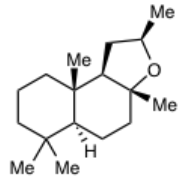


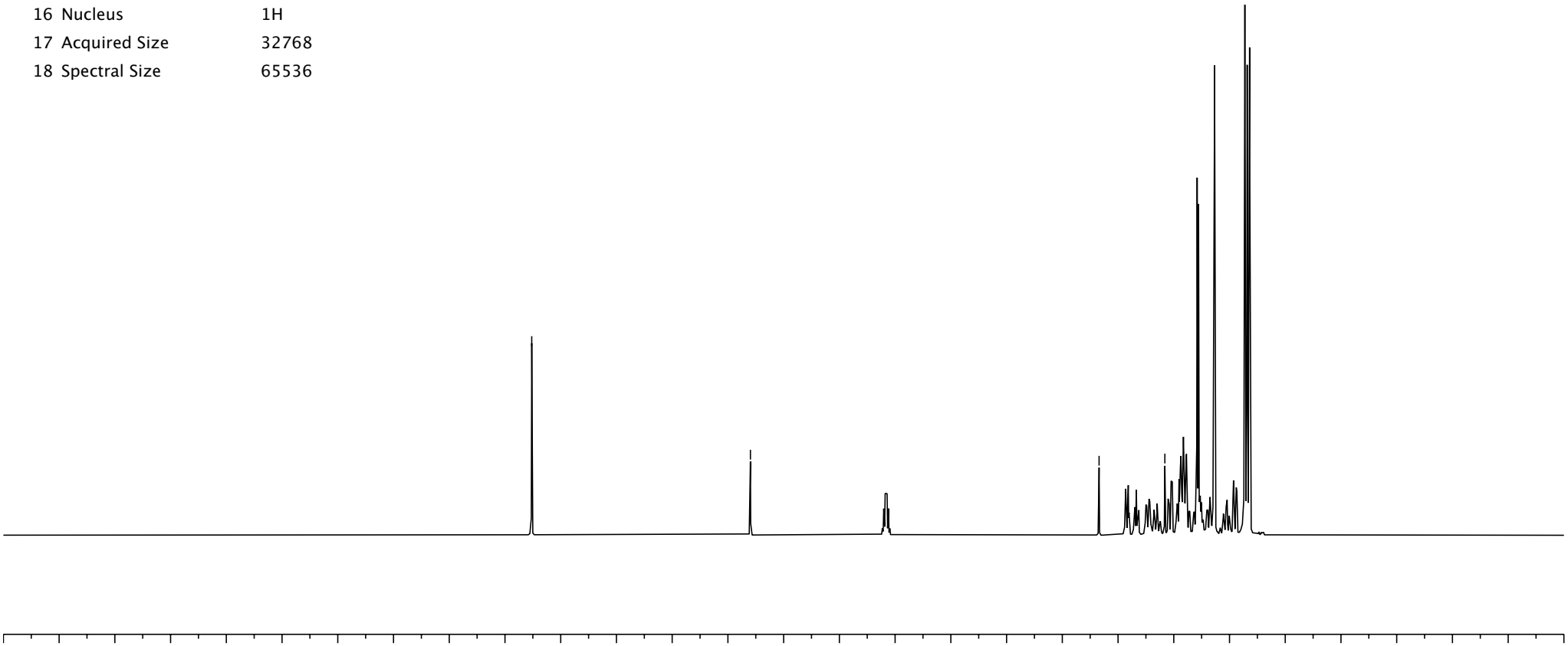


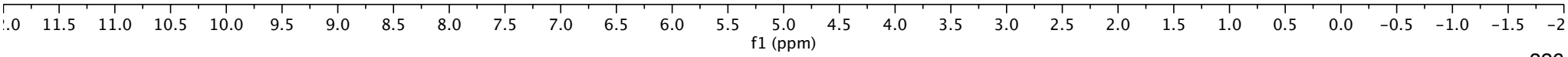
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1897.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



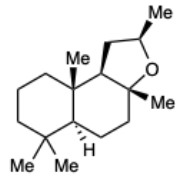
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.07
14	Spectral Width	8000.0
15	Lowest Frequency	-1521.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



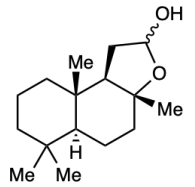




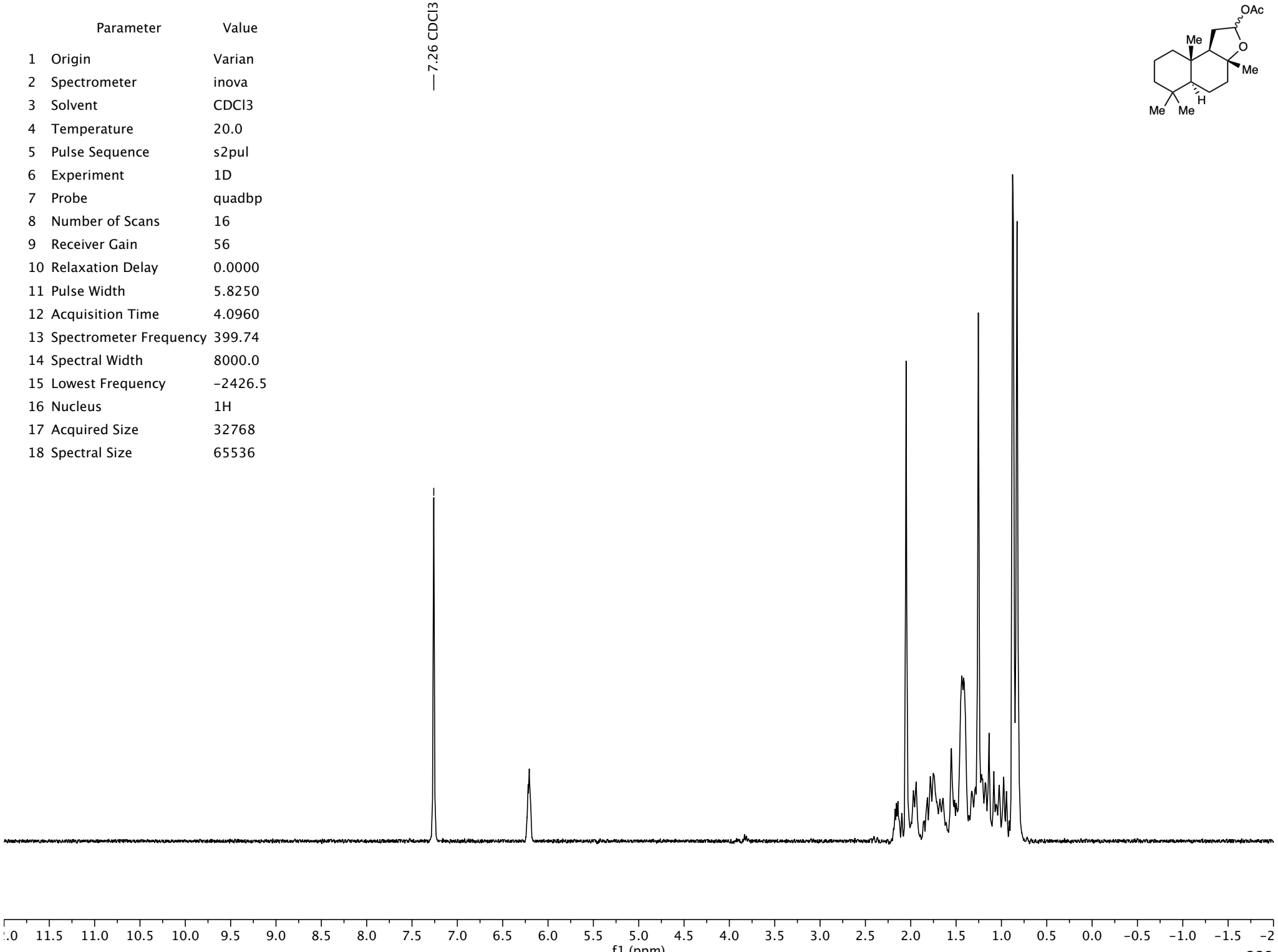
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1884.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



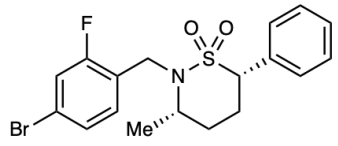
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



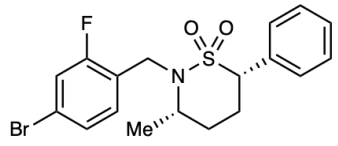
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	quadbp
8	Number of Scans	16
9	Receiver Gain	56
10	Relaxation Delay	0.0000
11	Pulse Width	5.8250
12	Acquisition Time	4.0960
13	Spectrometer Frequency	399.74
14	Spectral Width	8000.0
15	Lowest Frequency	-2426.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

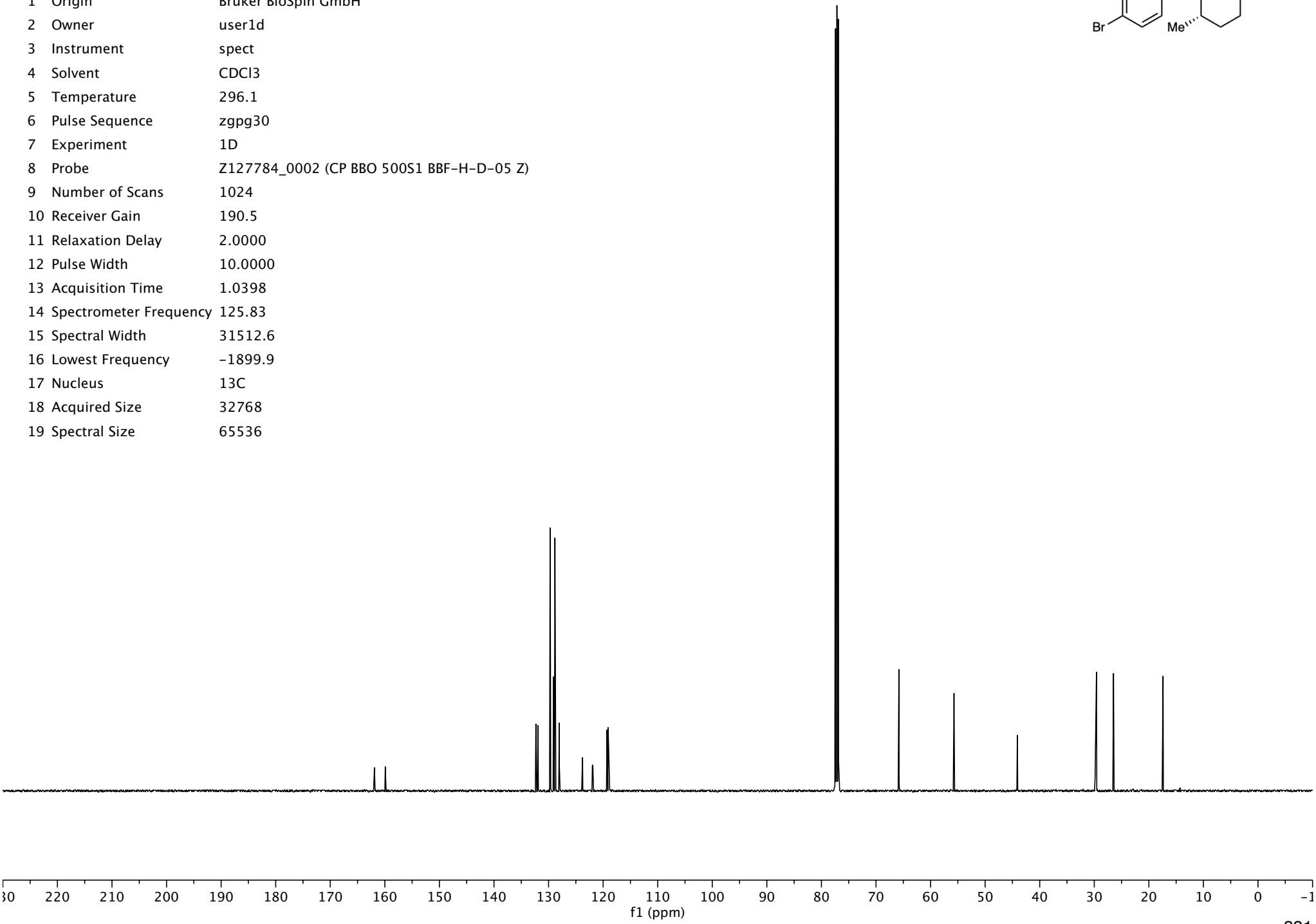


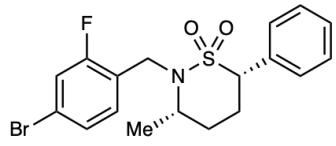
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	107.0
11	Relaxation Delay	16.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



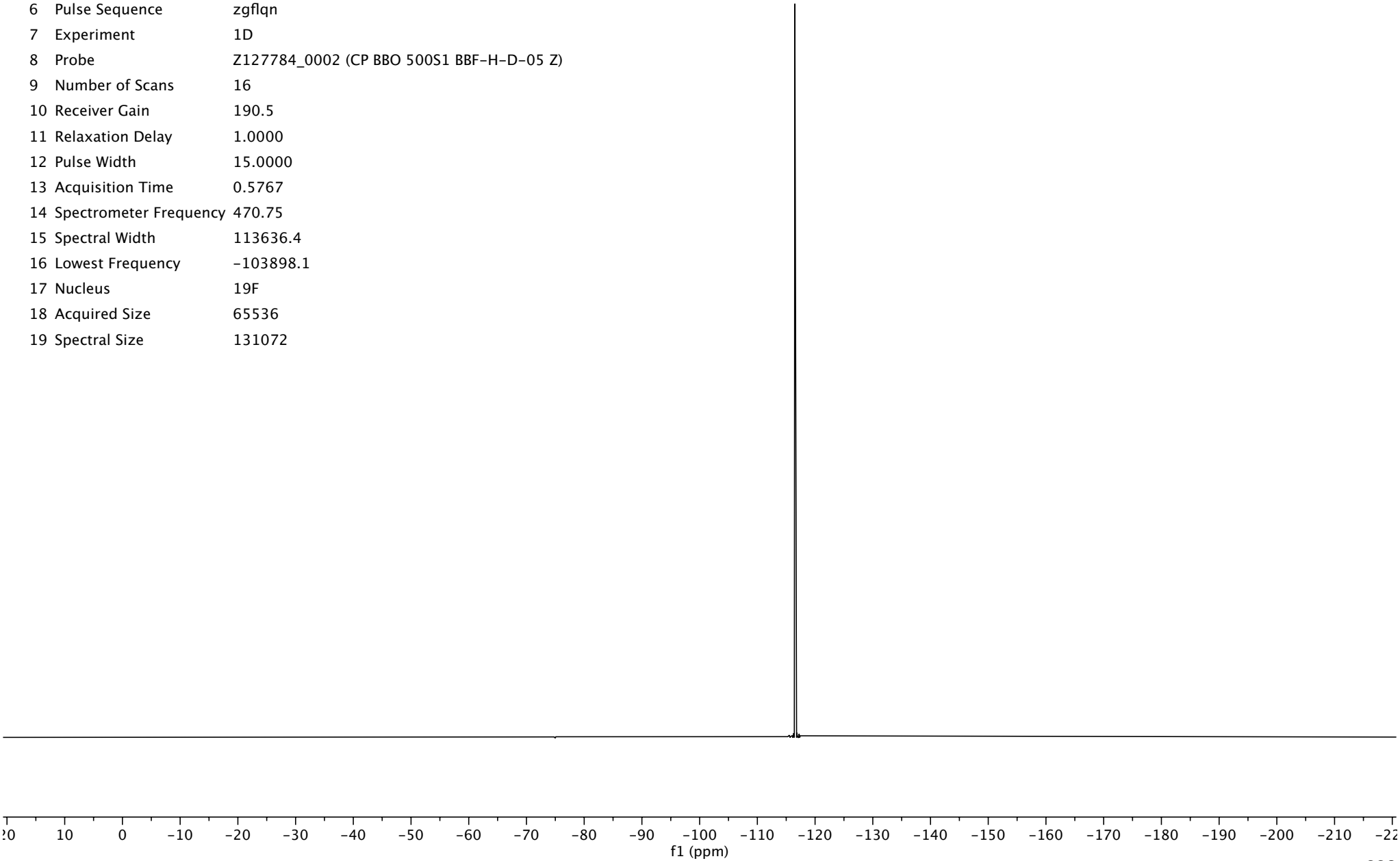
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Acquisition Time	1.0398
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

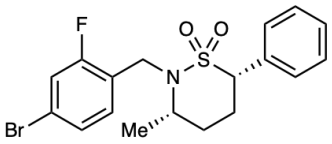




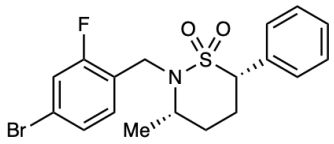


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Acquisition Time	0.5767
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

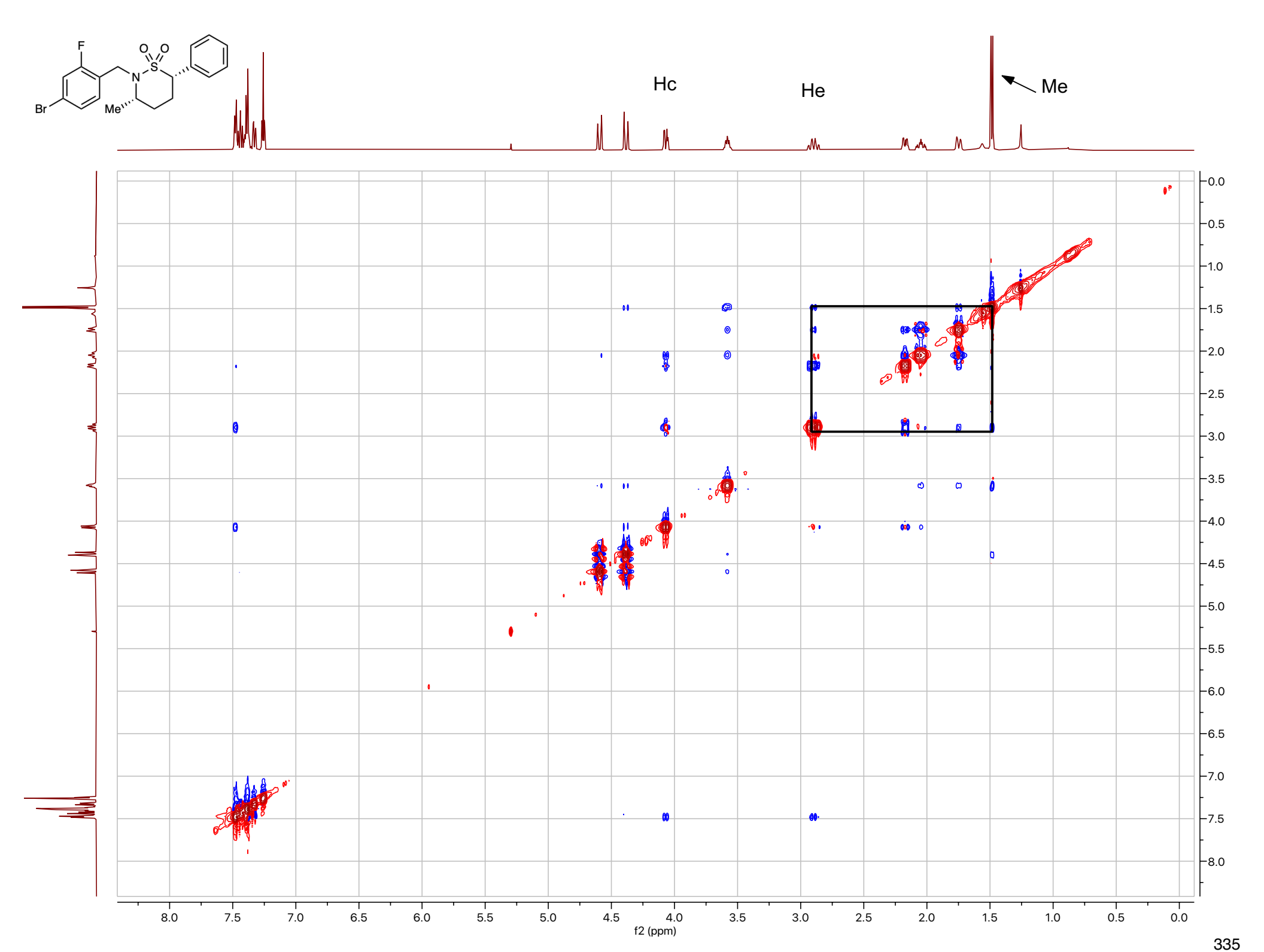




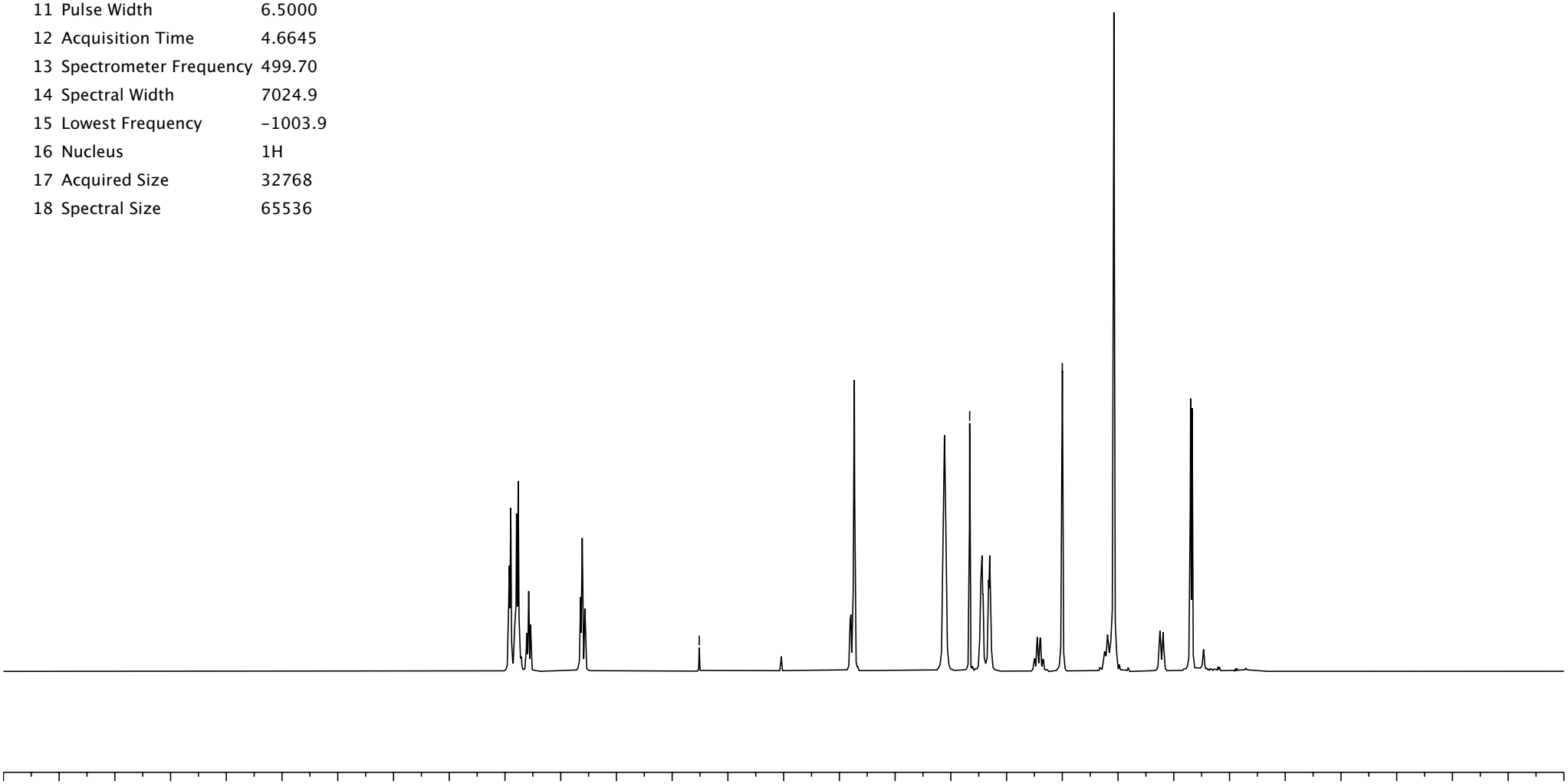
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	hsqcedetgp
7	Experiment	HSQC-EDITED
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2
10	Receiver Gain	190.5
11	Relaxation Delay	1.5000
12	Pulse Width	12.0000
13	Acquisition Time	0.1198
14	Spectrometer Frequency	(500.35, 125.82)
15	Spectral Width	(4273.5, 20746.9)
16	Lowest Frequency	(-63.2, -937.5)
17	Nucleus	(1H, 13C)
18	Acquired Size	(512, 256)
19	Spectral Size	(512, 512)



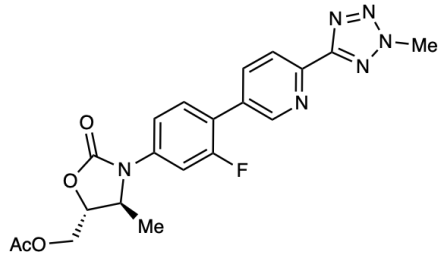
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	user1d
3 Instrument	spect
4 Solvent	CDCl3
5 Temperature	296.1
6 Pulse Sequence	cosygpppqf
7 Experiment	COSY
8 Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9 Number of Scans	1
10 Receiver Gain	61.8
11 Relaxation Delay	1.9177
12 Pulse Width	12.0000
13 Acquisition Time	0.2396
14 Spectrometer Frequency	(500.35, 500.35)
15 Spectral Width	(4273.5, 4273.5)
16 Lowest Frequency	(-63.2, -63.2)
17 Nucleus	(1H, 1H)
18 Acquired Size	(1024, 128)
19 Spectral Size	(1024, 1024)

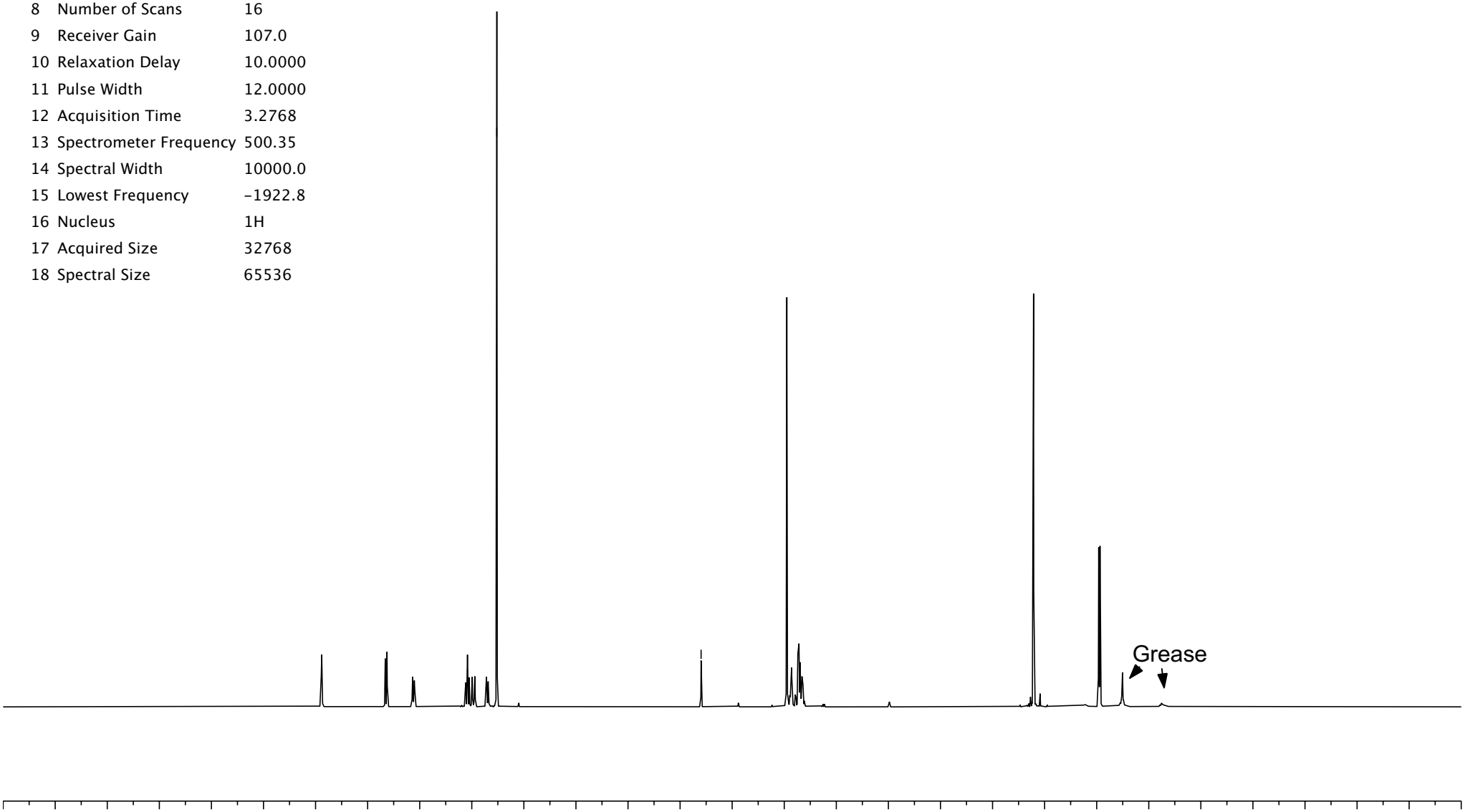

F
O
O
S
N
Br
Me
Hc
He
Me
f2 (ppm)

	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	DMSO
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	16
9	Receiver Gain	56
10	Relaxation Delay	10.0000
11	Pulse Width	6.5000
12	Acquisition Time	4.6645
13	Spectrometer Frequency	499.70
14	Spectral Width	7024.9
15	Lowest Frequency	-1003.9
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

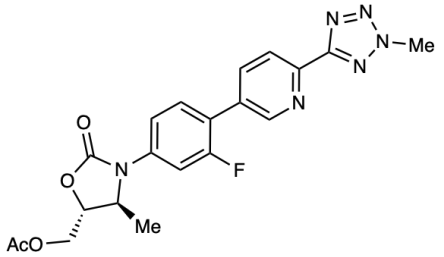


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	107.0
10	Relaxation Delay	10.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.8
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536





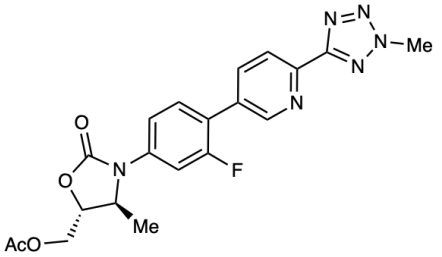
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1898.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

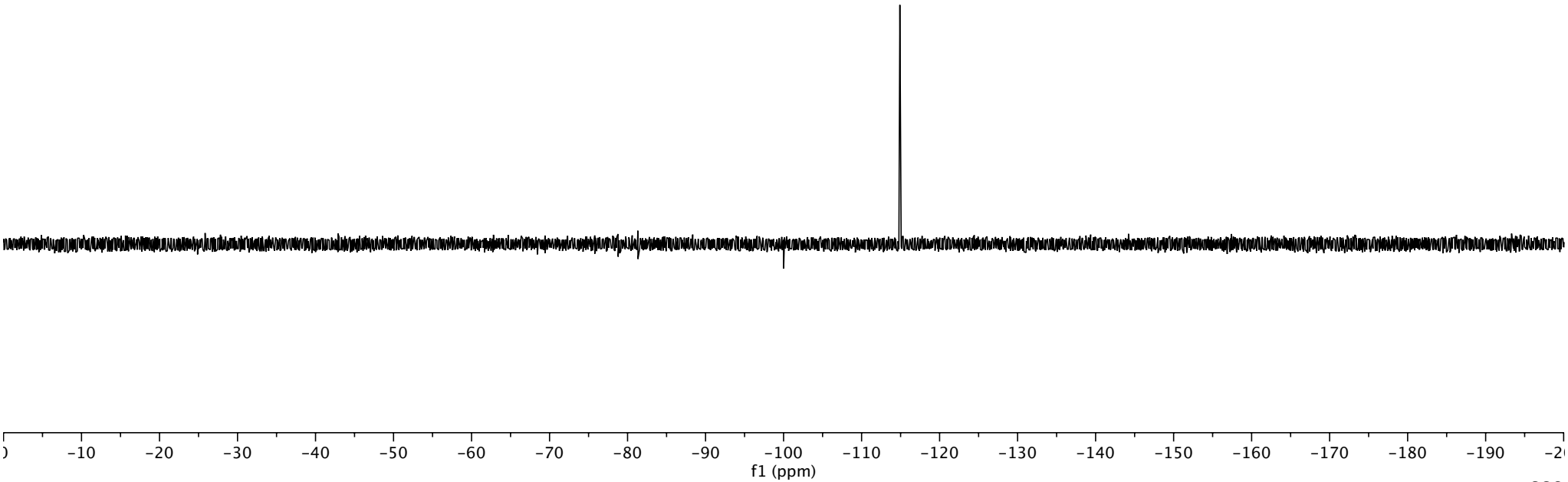


77.16 CDCl3

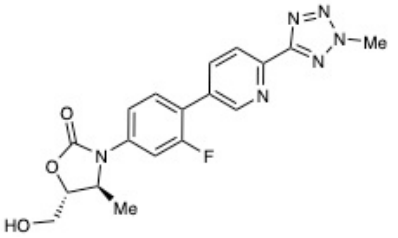
f1 (ppm)

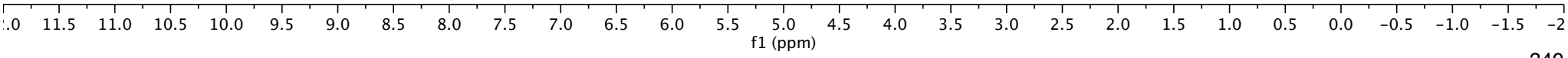
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Temperature	20.0
4	Pulse Sequence	s2pul
5	Experiment	1D
6	Probe	QUADG
7	Number of Scans	0
8	Receiver Gain	4
9	Relaxation Delay	1.0000
10	Pulse Width	33.0000
11	Acquisition Time	0.3277
12	Spectrometer Frequency	469.89
13	Spectral Width	94007.1
14	Lowest Frequency	-93996.9
15	Nucleus	19F
16	Acquired Size	30804
17	Spectral Size	65536



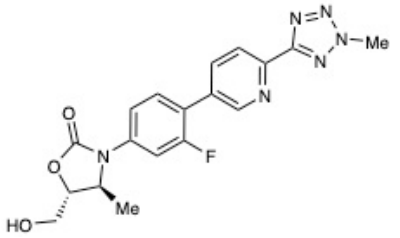


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1955.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536





	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1916.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



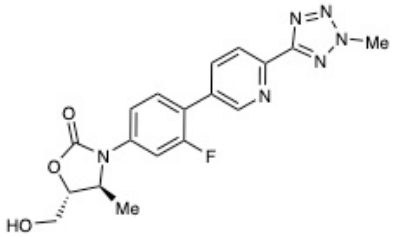
77.16 CDCl3

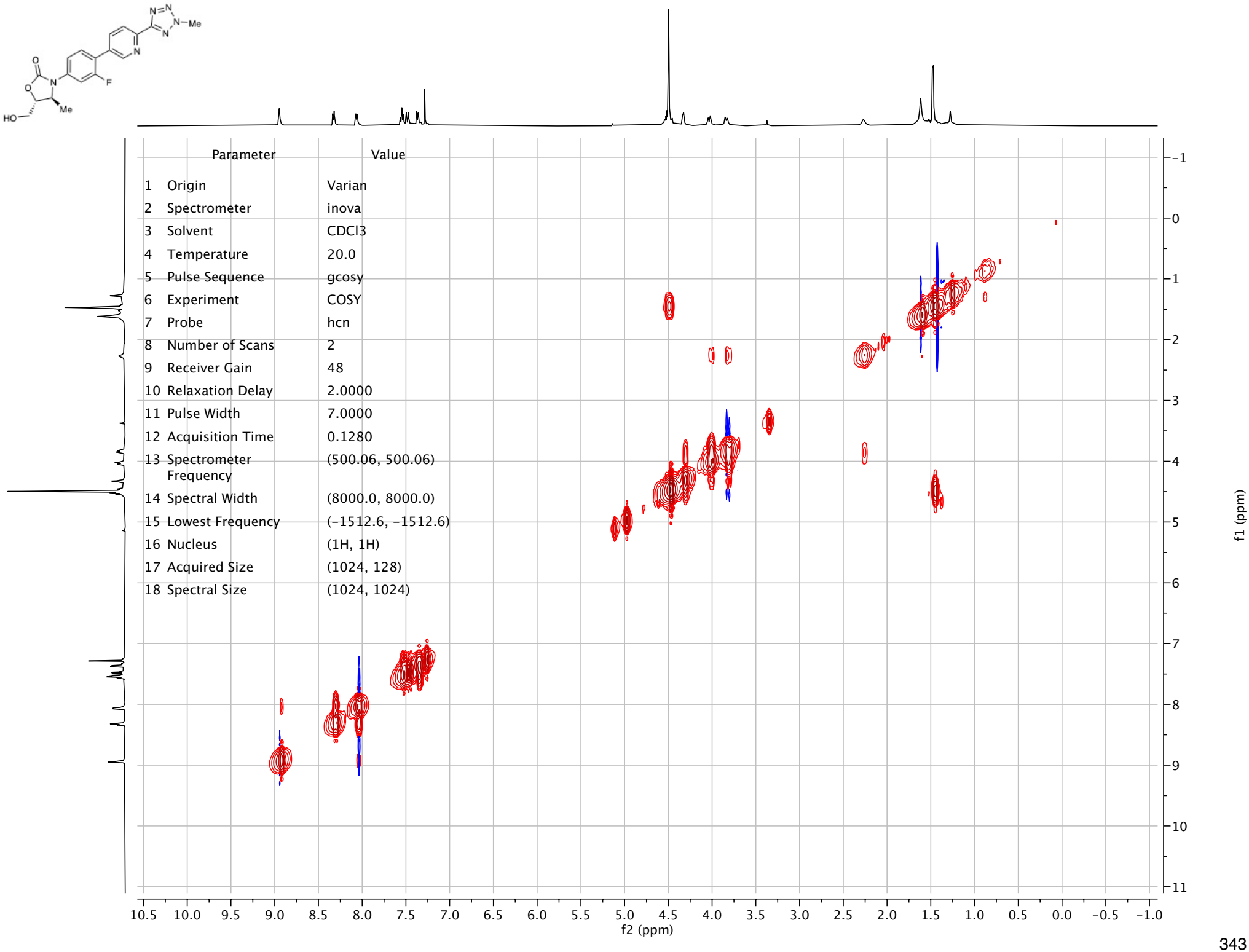
Grease

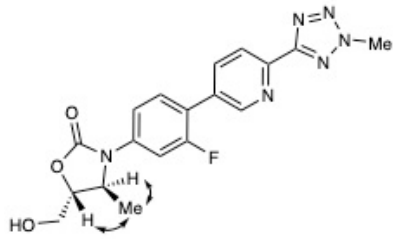
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	10.0000
11	Pulse Width	15.0000
12	Acquisition Time	0.5767
13	Spectrometer Frequency	470.75
14	Spectral Width	113636.4
15	Lowest Frequency	-103898.1
16	Nucleus	19F
17	Acquired Size	65536
18	Spectral Size	131072



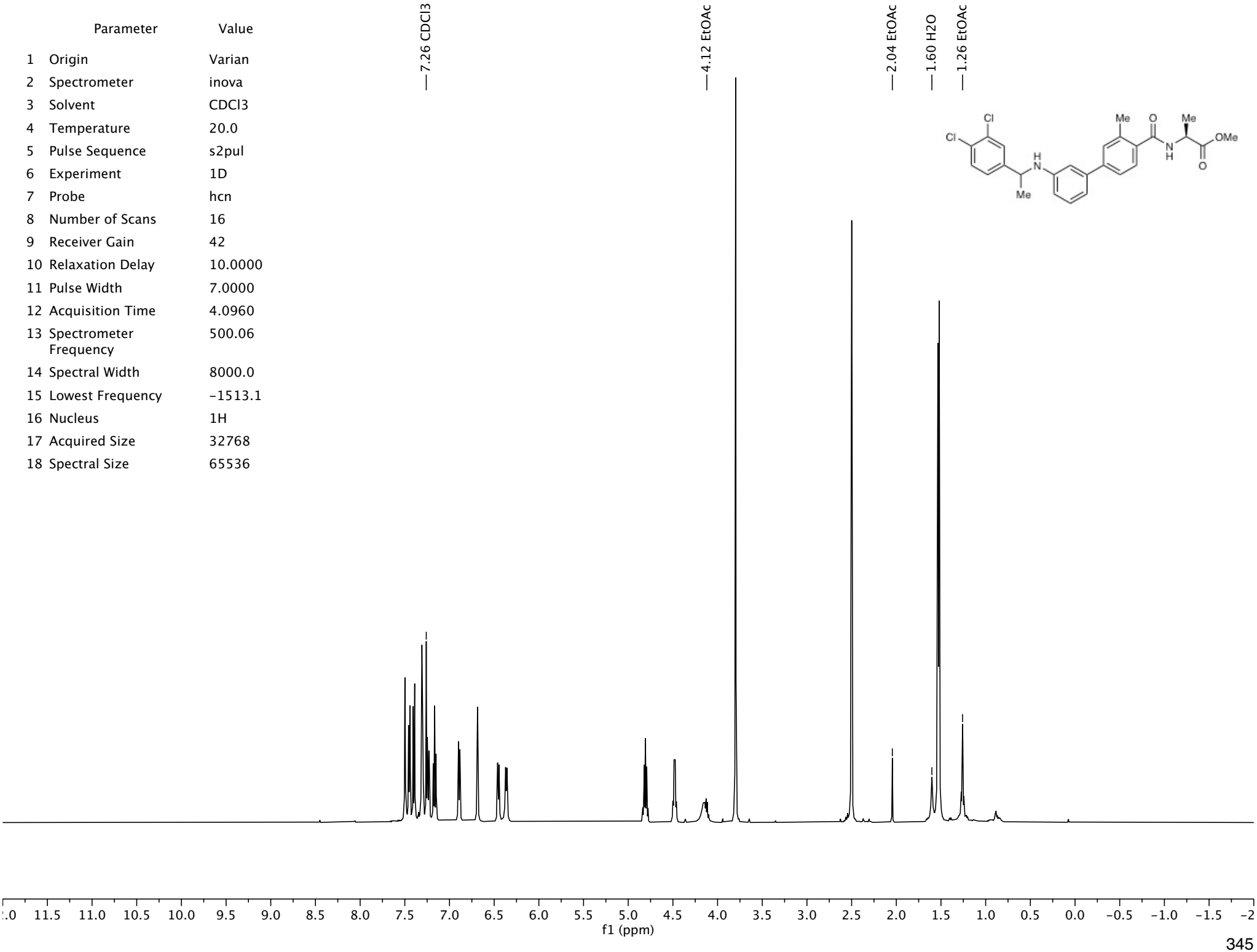

Parameter Value
1 Origin Varian
2 Spectrometer inova
3 Solvent CDCl3
4 Temperature 20.0
5 Pulse Sequence gcosy
6 Experiment COSY
7 Probe hcn
8 Number of Scans 2
9 Receiver Gain 48
10 Relaxation Delay 2.0000
11 Pulse Width 7.0000
12 Acquisition Time 0.1280
13 Spectrometer Frequency (500.06, 500.06)
14 Spectral Width (8000.0, 8000.0)
15 Lowest Frequency (-1512.6, -1512.6)
16 Nucleus (1H, 1H)
17 Acquired Size (1024, 128)
18 Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)



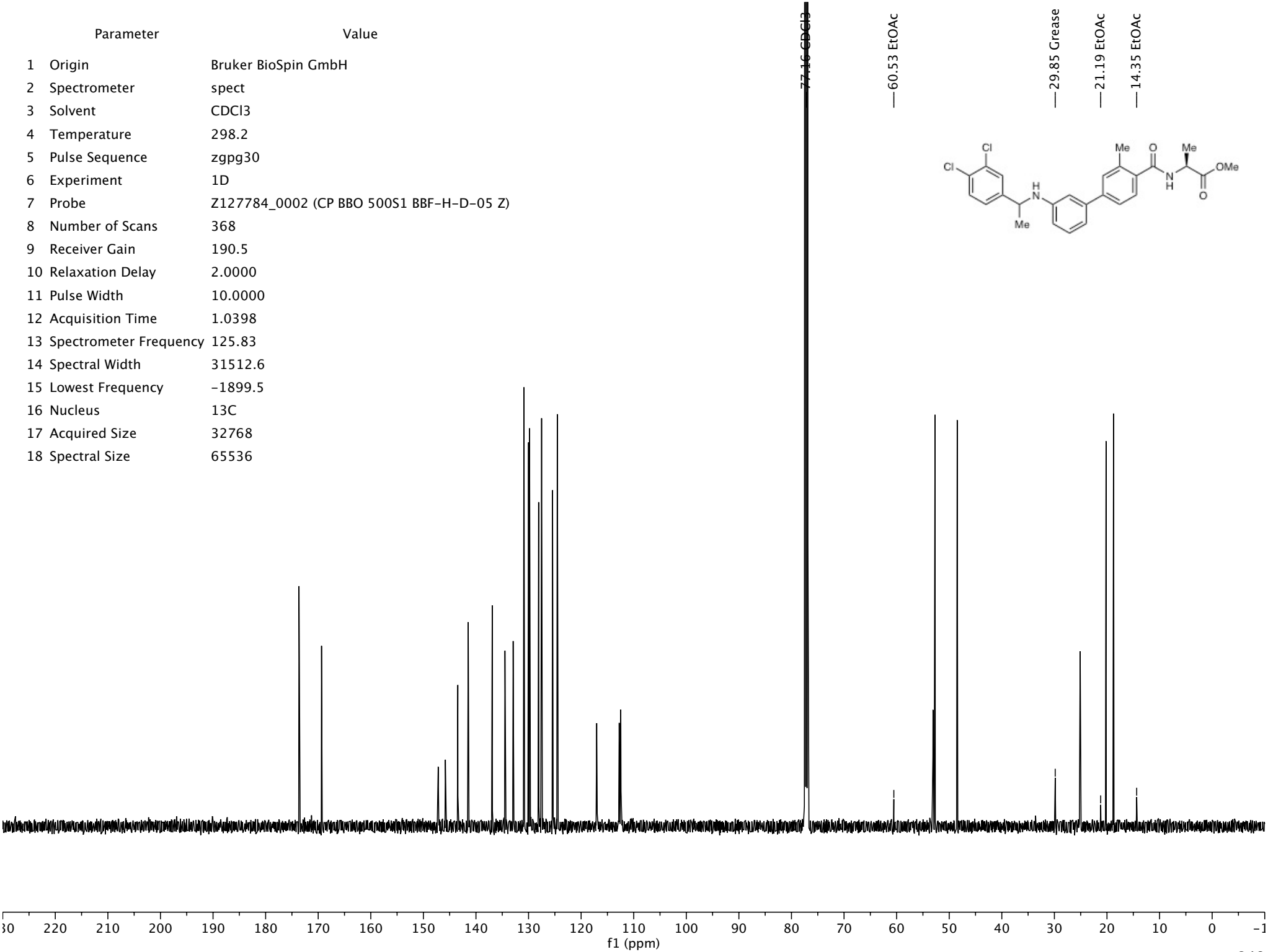
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

f1 (ppm)

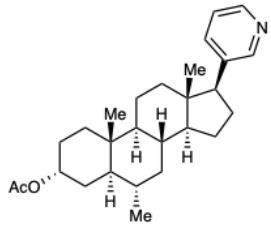
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	10.0000
11	Pulse Width	7.0000
12	Acquisition Time	4.0960
13	Spectrometer Frequency	500.06
14	Spectral Width	8000.0
15	Lowest Frequency	-1513.1
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



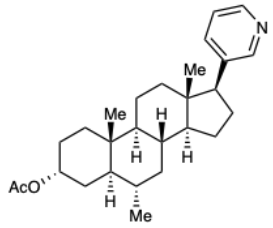
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

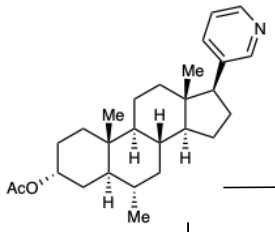


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	30.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1747.7
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

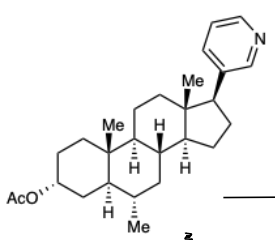


	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	22.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	416
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	6.0000
12	Acquisition Time	1.0863
13	Spectrometer Frequency	125.66
14	Spectral Width	30165.9
15	Lowest Frequency	-1273.5
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



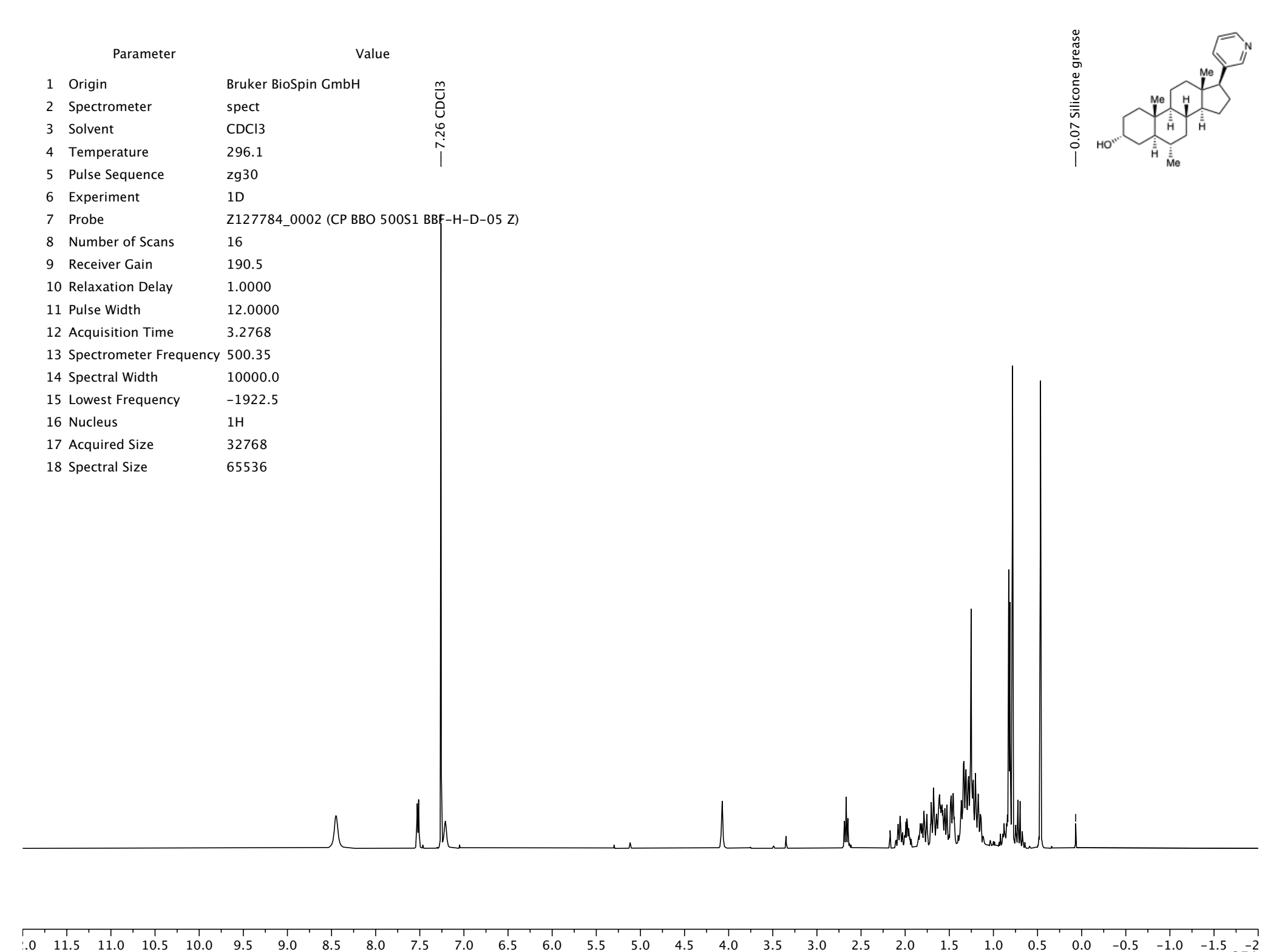


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	cosygpppqf
6	Experiment	COSY
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	1
9	Receiver Gain	61.8
10	Relaxation Delay	1.9545
11	Pulse Width	12.0000
12	Acquisition Time	0.2028
13	Spectrometer Frequency	(500.35, 500.35)
14	Spectral Width	(5050.5, 5050.5)
15	Lowest Frequency	(-298.6, -298.6)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)

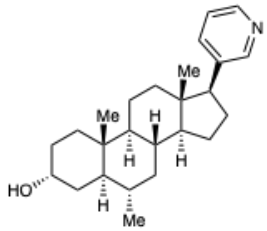


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	hsqcedetgp
6	Experiment	HSQC-EDITED
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	2
9	Receiver Gain	190.5
10	Relaxation Delay	1.5000
11	Pulse Width	12.0000
12	Acquisition Time	0.1014
13	Spectrometer Frequency	(500.35, 125.82)
14	Spectral Width	(5050.5, 20746.9)
15	Lowest Frequency	(-298.6, -937.5)
16	Nucleus	(1H, 13C)
17	Acquired Size	(512, 256)
18	Spectral Size	(512, 512)

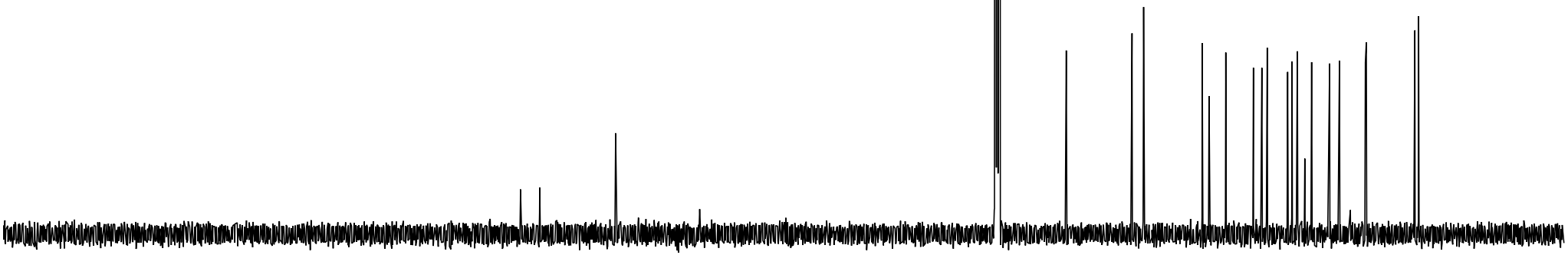
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	16
9	Receiver Gain	190.5
10	Relaxation Delay	1.0000
11	Pulse Width	12.0000
12	Acquisition Time	3.2768
13	Spectrometer Frequency	500.35
14	Spectral Width	10000.0
15	Lowest Frequency	-1922.5
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

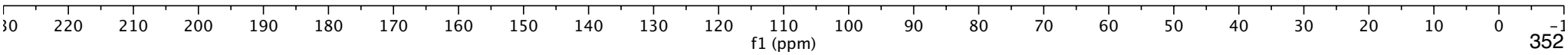


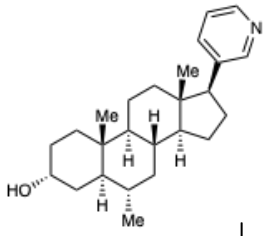
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
8	Number of Scans	368
9	Receiver Gain	190.5
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
12	Acquisition Time	1.0398
13	Spectrometer Frequency	125.83
14	Spectral Width	31512.6
15	Lowest Frequency	-1899.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536



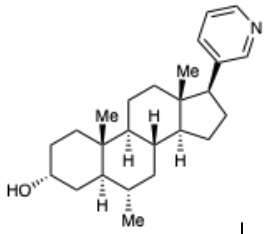
77.16 CDCl3



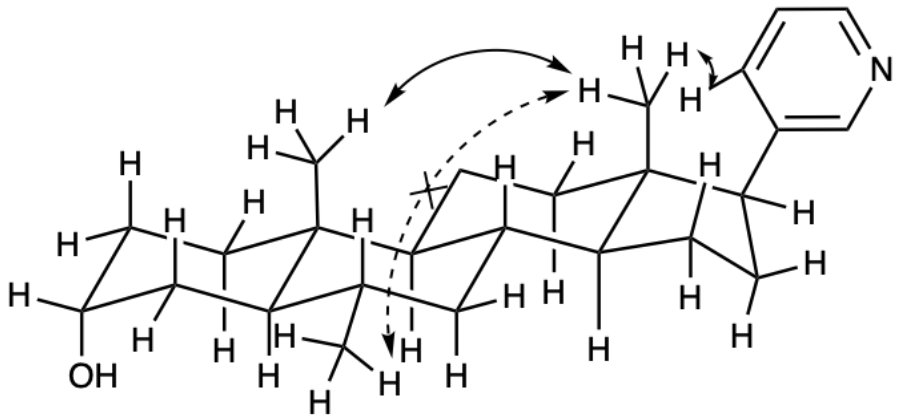


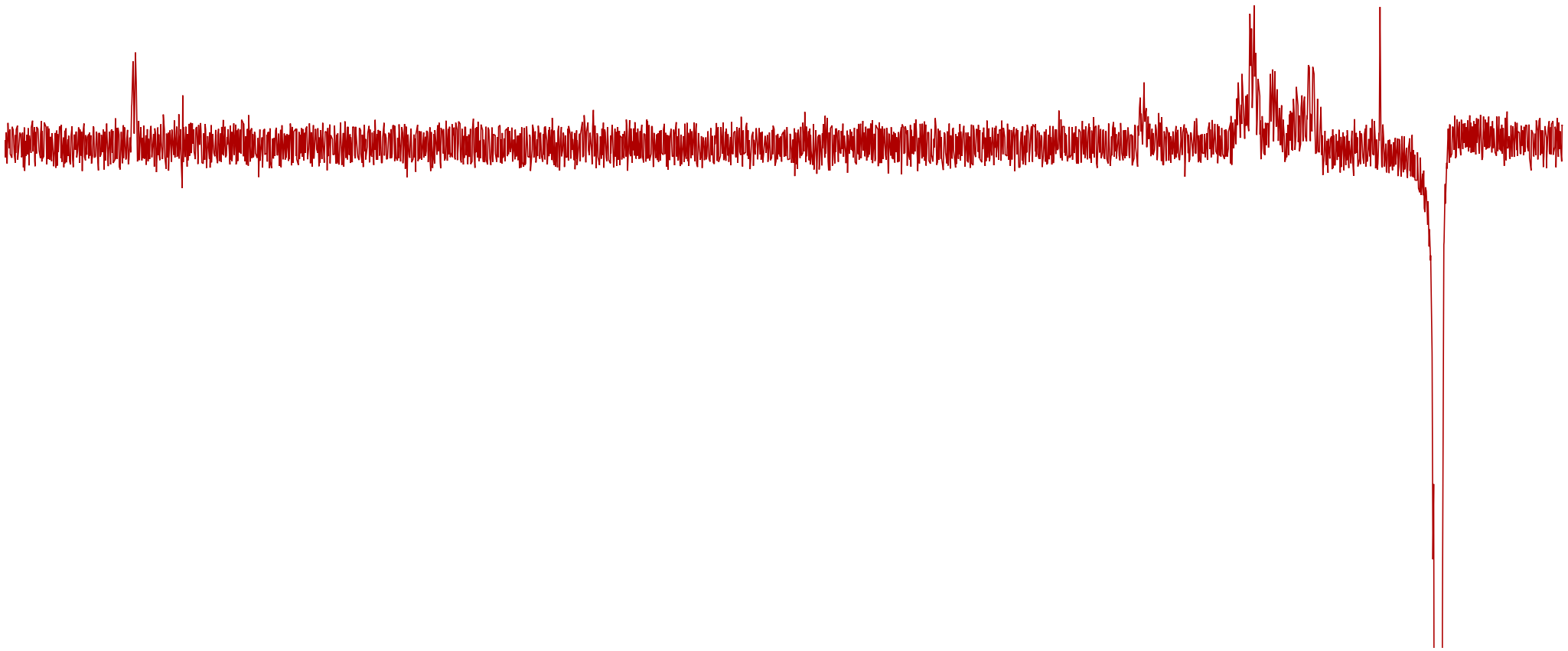


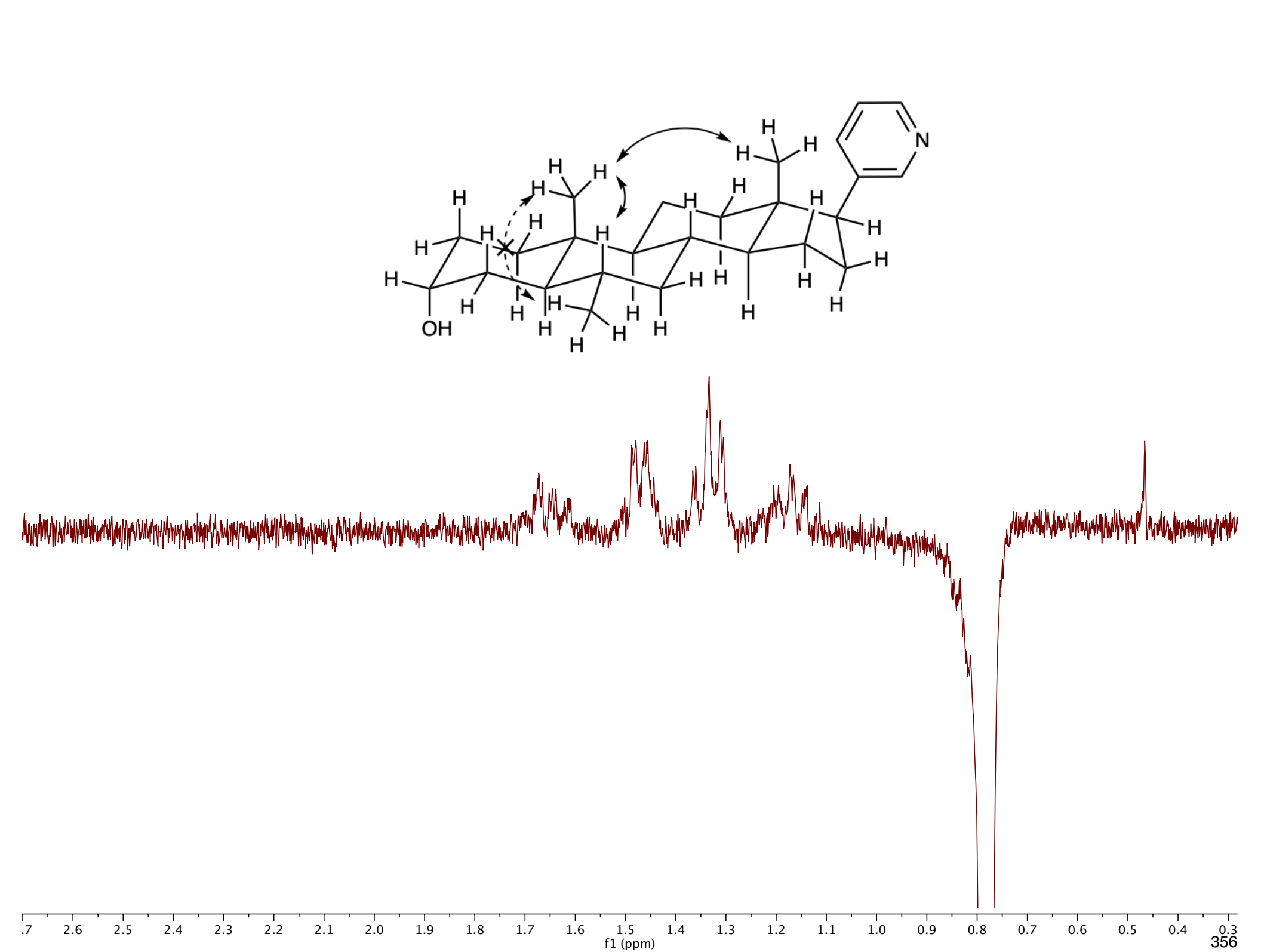
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	gcosy
6	Experiment	COSY
7	Probe	hcn
8	Number of Scans	2
9	Receiver Gain	44
10	Relaxation Delay	2.0000
11	Pulse Width	7.0000
12	Acquisition Time	0.1280
13	Spectrometer Frequency	(500.06, 500.06)
14	Spectral Width	(8000.0, 8000.0)
15	Lowest Frequency	(-1513.6, -1513.6)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)

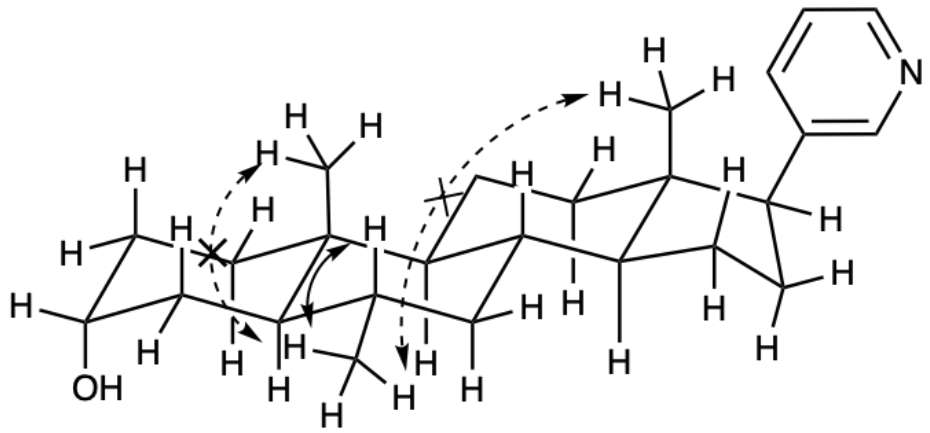


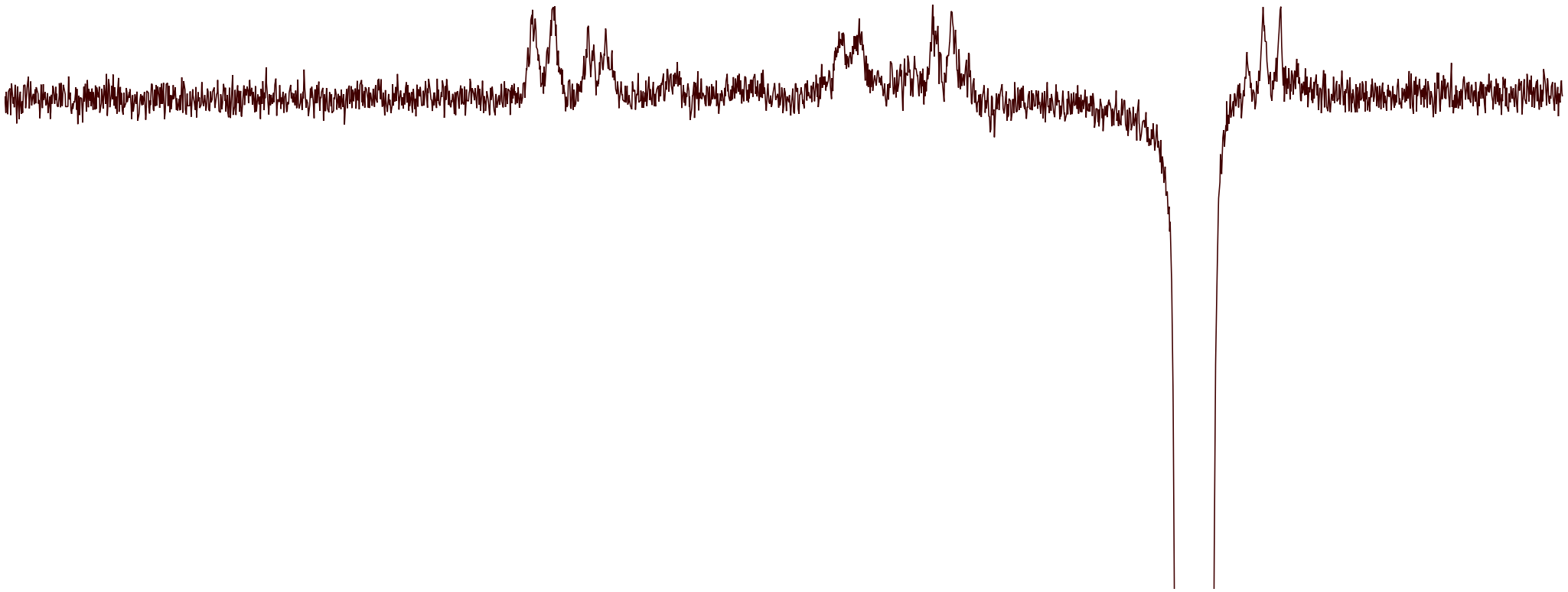
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	gcosy
6	Experiment	COSY
7	Probe	hcn
8	Number of Scans	2
9	Receiver Gain	44
10	Relaxation Delay	2.0000
11	Pulse Width	7.0000
12	Acquisition Time	0.1280
13	Spectrometer Frequency	(500.06, 500.06)
14	Spectral Width	(8000.0, 8000.0)
15	Lowest Frequency	(-1513.6, -1513.6)
16	Nucleus	(1H, 1H)
17	Acquired Size	(1024, 128)
18	Spectral Size	(1024, 1024)


H
N
OH


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
OH
f1 (ppm)


N
OH


2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
f1 (ppm)